

# Dipole glass and ferroelectricity in random-site electric dipole systems

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This review covers recent experimental and theoretical investigations into cooperative phenomena in crystals containing off-center ions. These phenomena have attracted much attention in recent years because of a general interest in disordered systems, in particular in spin glasses, whose electrical analog is the dipole glass. Specific features of the dipole glass state in alkali halide crystals with off-center ions are discussed and compared with spin glasses. Experimental studies performed in recent years have demonstrated that off-center ions in highly polarizable crystals can at certain concentrations induce ferroelectric domains with regions of macroscopic spontaneous polarization. The physical causes of this phenomenon are examined and some physical properties of crystals exhibiting such an impurity-induced phase transition are analyzed. Primary emphasis is placed on the range of low impurity concentrations, where system properties differ substantially from predictions of mean-field theory.

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## I. INTRODUCTION

The ordering of dipole particles, although a subject having a very long history, dating back to the studies of Langevin and Debye, has continued to be important up

to the present. This is particularly true of those systems containing impurities, which are highly sensitive to the effect of spatial "disorder," the random or irregular arrangement of the impurities. Thus, according to the Langevin-Debye theory, in which interaction between particles is described within the framework of an effective self-consistent field (the Lorentz field for dipole systems), a "polarization catastrophe," i.e., an unlimited increase in the polarizability of the system, resulting in a ferroelectric instability, should be expected as the temperature is lowered.

However, even the earliest experiments (Kanzig *et al.*, 1964; Peressini *et al.*, 1969; Fiory, 1970) with alkali halide crystals containing dipole impurities showed that nothing of this kind actually occurred; no ferroelectric phase transition was taking place. The explanation lies in the specificity of the dipole-dipole interaction potential: not only the magnitude, but also the sign of the interaction is strongly dependent on the relative orientations and positions of the dipoles. In systems containing impurities this in turn leads to considerable fluctuation of local fields acting on various dipoles due to adjacent impurities, with the result that the approximation of a homogeneous self-consistent field becomes invalid. Although early theoretical studies (Zernic, 1965, 1967) attempted to describe experiments on the basis of various versions of the self-consistent field method, neglecting spatial fluctuations of particles, it became clear from subsequent analysis (Klein, 1966; Lawless, 1966a, 1966b) that such fluctuations greatly reduce the effective polarizability and therefore prevent the onset of ferroelectric instability.

It may now be regarded as established that, due to a great spread of local fields at various crystal points, dipole moments at low temperatures get frozen into random orientations, with a total absence of ferroelectric long-range order. The situation then strongly resembles that occurring in CuMn-type dilute magnetic alloys, where localized magnetic moments coupled by a varying-sign exchange interaction give rise to a spin-glass state characterized by random orientations of magnetic moments with zero total magnetization. Alkali halide crystal-type dielectrics with dipole impurities can therefore be considered as electrical analogs of spin glasses

and are generally called dipole glasses. Although a truly equilibrium behavior of dipole glass, as well as many of spin glasses, has not been fully revealed so far, the observed low-temperature properties can be qualitatively described by use of the concept of long-lived metastable states, in which every dipole is oriented along the random local field acting upon it.

The question of the nature of ordering in crystals containing dipole impurities has recently been raised again in view of the discovery of impurity dipoles in the highly polarizable dielectric  $\text{KTaO}_3$ . Thus Vugmeister and Glinchuk (1980) demonstrated that the possibility of a ferroelectric phase transition in such compounds is increased by spatial dispersion of permittivity, which is usually considerable in highly polarizable media. The existence of spatial dispersion, characterized by the polarization correlation radius  $r_c$ , changes the effective interaction potential between dipoles so that the interaction between impurities separated by distances  $r < r_c$  turns out to be predominantly ferroelectric and more complicated than is the usual dipole-dipole interaction; hence the interaction is not specifically a dipole one. Because of the specific nature of the interaction, configurational fluctuations of local fields (which prevent the ferroelectric phase transition in weakly polarizable alkali halide crystals) decline, and a long-range order can appear in the system at high enough impurity concentrations. A dipole glass phase can also form under certain conditions.

Which of the above-mentioned ordering types does occur? This question has been the subject of numerous arguments and discussions continuing to the present day. It can nevertheless be stated by now that the situation in highly polarizable crystals is radically different from that in traditional dipole glasses, and quite a number of experiments show convincing evidence for the occurrence of dipole impurity-induced ferroelectric phase transitions.

The most typical representatives of dipole impurities exhibiting cooperative properties are off-center ions, the so-called substitutional impurity ions, whose equilibrium positions are displaced from a lattice site. It is clear that an off-center impurity/vacancy (due to an absent site atom) set in an ionic crystal has an effective electric dipole moment. The direction of such dipoles, i.e., the position of an ion, which may have several positions, is not random, but is determined by the crystal symmetry. Thermal or tunnel jumps between various positions may occur. Therefore the dipoles are not frozen and, like dipole molecules, such as  $\text{OH}^-$ , can be oriented by both external and internal electric fields, which is the prerequisite for the appearance of temperature-dependent cooperative effects.

The first off-center ion to be detected was  $\text{Li}^+$  in  $\text{KCl}$  (Lombardo and Pohl, 1965). After this, off-center ions were found in many other substances, including not only classical dielectrics, such as alkali halide and alkaline-earth crystals, but also more complex compounds undergoing structural phase transitions or being near the sta-

bility threshold. The appearance of the off-centrality was as a rule encouraged by the great difference between ionic radii and polarizabilities of substituent and substituted atoms, upsetting the balance of polarization and repulsive forces at the centrally symmetric point of the unit cell.

The presence of off-center ions changes considerably the crystal properties, giving rise to anomalies in the specific heat, thermal conduction, and sound absorption, as well as to specific features in Raman and infrared spectra and to changes in electric, dielectric, magnetic, and other properties. The research conducted to date has been partly systematized in reviews by Narayanamurti and Pohl (1970), Dejgen and Glinchuk (1974), Barker and Sievers (1975), Bridges (1975), and Kopvillem and Saburova (1982). These reviews, however, are primarily confined to discussing individual properties of off-center ions and their independent individual effects on the host crystal. In contrast, the present review will focus attention on features of cooperative phenomena stemming from the interaction of impurity dipoles.

This review will therefore be aimed at discussing the principal features of cooperative behavior of dipole impurities in dielectric crystals. We shall not consider the so-called structural glasses in polar materials, such as ADP-RDP systems, which are dealt with in numerous publications [e.g., the reviews of Courtens (1983, 1985)]. The term "dipole glasses" will further imply systems containing dilute impurities and featuring dipole-dipole interaction forces, i.e., only the cooperative behavior of dipole impurities in dielectric crystals will be dealt with. Due to the similarity of such systems to magnetic spin glasses, the opinion is often expressed that dipole glasses are fully analogous to spin glasses, and general propositions of spin-glass theory are sometimes even illustrated by use of an example from the dipole glasses (Binder and Young, 1986). One of the objectives of this review is to demonstrate a certain specificity existing here and to attract the attention of readers to this problem. In particular, no experimental data for dipole glasses give evidence of the occurrence of an equilibrium phase transition to the state of dipole glass. This was most clearly shown by measurements of nonlinear dielectric susceptibility (Saint-Paul and Gilchrist, 1986). The experiment detected no critical growth of the susceptibility, as is the case in spin glasses such as  $\text{CuMn}$  and others; hence the situation in dipole glasses differs radically from that occurring in classical spin glasses. Such a difference appears to stem from the specificity of the dipole-dipole interaction potential, since recent experiments with magnetic dipole glasses (Reich *et al.*, 1986) likewise revealed no indications of an equilibrium phase transition to the state of dipole spin glass.

This review has a limited goal: to consider a specific class of systems with dipole impurities in dielectric crystals. The authors therefore have deliberately avoided repeating information that can be found in other reviews and, on the contrary, have tried to cover those aspects of

the problem which were dealt with only a little or not at all in other reviews.

We did not set ourselves the task of discussing various theoretical models of spin glasses (as applied to dipole glasses). This has already been done in sufficient detail in other reviews (Fischer, 1983; Binder and Young, 1986) and besides, as mentioned above, applying spin-glass models to dipole glass fails to explain many observed phenomena. Rather, we tried to show that specific properties of dipole glass stem from the specificity of the potential of the dipole-dipole interaction at a random arrangement of particles. This, as will be seen, makes it possible within the framework of a single formalism to trace the changes in system properties with varying dipole-dipole interaction potential in highly polarizable crystals.

The review includes a discussion of experimental and theoretical studies of the dipole-glass state in alkali halide crystals (Sec. II). The causes of the appearance of ferroelectric ordering in highly polarizable crystals containing dipole impurities (off-center ions) are presented in Sec. III. Section IV deals with the results of experimental and theoretical research into specific features of such crystals. In the Appendix, by the use of some model systems, the random-local-field method which is employed in this review is tested, and, as will be shown below, makes it possible to understand at a qualitative and semi-quantitative level many distinguishing features of disordered dipole systems.

## II. DIPOLE GLASS IN WEAKLY POLARIZABLE DIELECTRICS CONTAINING DIPOLE IMPURITIES

This section will discuss the effect of dipole forces acting between off-center ions and other similar impurities on low-temperature properties of weakly polarizable dielectrics whose typical representatives are alkali halide crystals.

### A. Observed properties

We begin by discussing typical experimental results in which characteristic properties of dilute dipole systems show up most markedly.

#### 1. Dielectric susceptibility

The first observations of dielectric properties in dilute dipole systems were described by Kanzig, Hart, and Roberts (1964). This study was then substantially extended and generalized by Fiory (1970), who investigated KCl:Li, NaBr:F, KCl:OH, and RbCl:OH systems. These studies have recently been continued by Potter and Anderson (1981a, 1981b), Moy *et al.* (1983), Saint-Paul *et al.* (1983), de Yoreo *et al.* (1984), and Saint-Paul and Gilchrist (1986).

All the systems studied by the above exhibit a similar

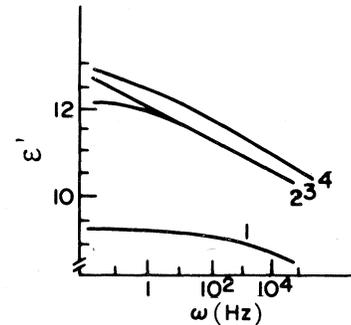


FIG. 1. Real part of permittivity of KCl:Li as a function of frequency  $\omega$  ( $n = 3 \times 10^{18} \text{ cm}^{-3}$ ). Values for  $T$  (K): curve 1, 1.5; curve 2, 0.8; curve 3, 0.25; curve 4, 0.4. After Fiory, 1970.

behavior. When impurities are introduced, permittivity  $\epsilon$  increases and becomes strongly dependent on frequency (Fig. 1). As can be seen, the permittivity decreases monotonically with increasing frequency in the range from  $10^{-2}$  to  $10^5$  Hz, which indicates a considerable spread in relaxation times. At not-too-low temperatures, however, the frequency dispersion of  $\epsilon$  practically ceases at frequencies of about  $10^{-2}$  Hz, and therefore the temperature anomalies in  $\epsilon$ , observed at these frequencies (Fig. 2), may be regarded as not resulting from the usual relaxation effects.

Figure 2 shows the temperature dependence of the excess permittivity  $\Delta\epsilon = \epsilon - \epsilon_0$  of KCl:Li for various concentrations of off-center ions. As can be seen from Fig. 2, at high temperatures  $\Delta\epsilon$  is directly proportional to the concentration of lithium dipoles and it decreases with temperature as  $T^{-1}$  in accordance with the Langevin-Debye law. At low concentrations of off-center ions, the effects of interactions do not show up at all, and the behavior of  $\Delta\epsilon$  is determined by the magnitude of the tunneling splittings. As the concentration is increased, a maximum appears in the temperature dependence of  $\Delta\epsilon$ , becoming sharper at higher concentrations. The temperature  $T_m$  of the maximum of  $\Delta\epsilon$ , determined by Fiory (1970) for various dipole systems, is proportional to the

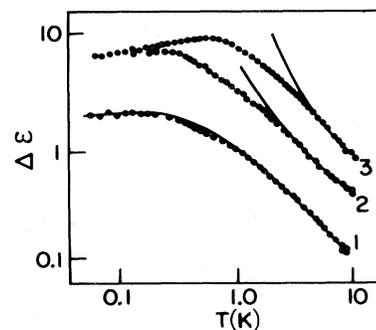


FIG. 2. Temperature dependence of permittivity excess  $\Delta\epsilon$  of KCl:Li. Values for  $n$  ( $\text{cm}^{-3}$ ): curve 1,  $10^{18}$ ; curve 2,  $4.5 \times 10^{18}$ ; curve 3,  $10^{19}$ . Solid curves were calculated from Eq. (2.2). After Fiory, 1970.

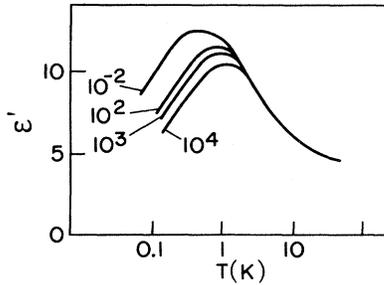


FIG. 3.  $\epsilon''(T)$  in  $\text{KCl:OH}^-$  (Fiory, 1970; Medina *et al.*, 1984).

mean energy of the dipole-dipole interaction and approximately corresponds to the relation

$$kT_m \approx nd^2/\epsilon_0, \tag{2.1}$$

where  $n$  is the concentration of impurities and  $d^*$  is their effective dipole moment with allowance for the Lorentz field correction. In simple cubic crystals,  $d^* = (\epsilon_0 + 2)d/3$ , where  $d$  is the intrinsic dipole moment, determined by the off-center displacement magnitude.

Figure 2 also shows that the excess permittivity values observed at  $T > T_m$  are considerably lower than those predicted by the self-consistent mean-field theory in the form of the Clausius-Mossotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} + \frac{4\pi}{3} n\chi_0, \tag{2.2}$$

where  $\chi_0 = (2d^2/3\Delta)th(\Delta/2kT)$  is the single-particle polarizability of noninteracting impurities and  $\Delta$  is the tunneling energy (for Li in KCl,  $\Delta/k_B \sim 1$  K). These results can be explained only if  $\chi_0$  in Eq. (2.2) is replaced with  $\chi_0(1 - (B/T))$ , where  $B \approx T_m$ . Hence the high-temperature behavior of permittivity clearly shows that the dipole correlations reduce the polarizability of the system and therefore prevent the ferroelectric instability ( $\epsilon \rightarrow \infty$ ) allowed by Eq. (2.2).

Figure 3 presents the dielectric susceptibility in the  $\text{KCl:OH}^-$  system (Medina *et al.*, 1984). Since for  $\text{OH}^-$  molecules the tunneling splitting value is  $\Delta/k_B \ll 1$  K,

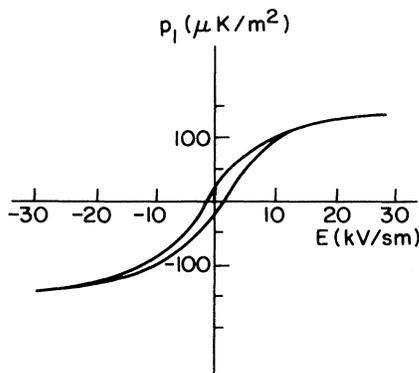


FIG. 4. Hysteresis loop of  $\text{KCl:Li}$  ( $T=0.06$  K;  $n=3 \times 10^{18}$   $\text{cm}^{-3}$ ). After Fiory, 1970.

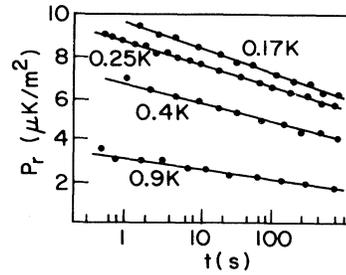


FIG. 5. Residual polarization in  $\text{KCl:Li}$  as a function of time (Fiory, 1970).

the  $\epsilon$  maximum is more pronounced than that in Fig. 2. The frequency dependence of the temperature of the maximum is adequately described as  $T_m \propto -1/\ln(\omega/\nu)$ .

### 2. Residual polarization

The observed (Fiory, 1970) hysteresis loop and residual polarization are direct evidence that interacting impurity dipoles can orient one another. The effect becomes appreciable at  $n > 10^{18}$   $\text{cm}^{-3}$  and temperatures below 0.3 K. A typical hysteresis curve is shown in Fig. 4. At higher temperatures the loop area decreases, and at  $T > 1$  K the hysteresis vanishes altogether. The hysteresis loop shape is quite different from that observed for ferroelectrics. Moreover, the residual polarization ( $P_r \approx 10\%nd^*$ ) as well as the coercive field are very small in comparison with ferroelectrics.

Hysteresis has been found to be accompanied by a heat release both when the electric field is increased and when it is reduced. At low temperatures, the heat release due to the hysteresis impeded the observation of the electrocaloric effect, which was investigated at higher temperatures by Kapphan and Lüty (1968).

The residual polarization has also been measured after cooling the specimens in an electric field and then turning off the field. Figure 5 shows the time dependence of the residual polarization to be logarithmic. The polarization decays very rapidly initially, but then varies very slowly. The dependence of the residual polarization on the dipole concentration is close to quadratic,  $P_r \propto n^2$  (see Fig. 6).

### 3. Specific heat

The temperature behavior of the specific heat changes with increasing concentration of off-center ions. For  $\text{KCl:Li}$ , a maximum due to the presence of tunneling states exists at low concentrations (Peressini *et al.*, 1969), but at higher concentrations the specific heat increases monotonically with temperature over the entire attainable temperature range. No marked anomalies have been found near  $T_m$ . The temperature range of the measurements was, however, limited, since the contribution by

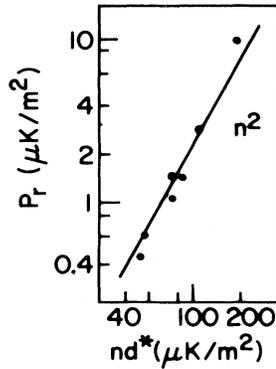


FIG. 6. Concentration dependence of residual polarization in KCl:Li ( $t = 60$  s;  $T = 0.2$  K). After Fiory, 1970.

the lattice specific heat, which increases approximately at  $T^3$ , begins to predominate at higher temperatures. Due to the high specific heat of the tunneling states, highly concentrated samples had to be selected to observe the interaction effects. Beginning from a concentration  $n \approx 7 \times 10^{18} \text{ cm}^{-3}$ , the low-temperature behavior of the specific heat followed the relation (Fiory, 1970)

$$C_v \propto n^{-1/2} T^{3/2}. \quad (2.3)$$

Using an analogy with ferromagnets, where the relation  $C_v \propto T^{3/2}$  is due to the contribution of spin waves, Fiory (1970) suggested that polarization-waves may exist in dilute dipole systems, but his detailed studies revealed no indications of the existence of such collective excitations.

More detailed measurements of the specific heat were conducted for the KCl:OH<sup>-</sup> system by de Yoreo and Pohl (1984; see also Kapphan and Lüty, 1968). A diffuse maximum, typical for disordered systems, was observed, whose temperature somewhat exceeded that of the permittivity maximum (de Yoreo and Pohl, 1984). At an atomic concentration  $X_{\text{OH}^-} = 0.1\%$  the low-temperature behavior of the specific heat is fairly accurately described by the relation  $C_v \propto T^{3/2}$ , but at  $X_{\text{OH}^-} = 0.2\%$  (Fig. 7),  $C_v \propto T$  over a wide temperature range.

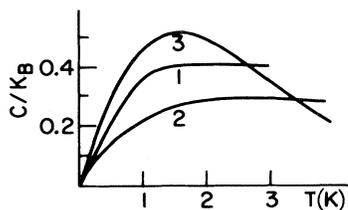


FIG. 7. Comparison of calculated specific-heat values with experimental results and theoretical predictions: Curve 1, experiment (de Yoreo *et al.*, 1984); curve 2, calculations of Vugmeister; curve 3, theoretical predictions of Klein *et al.*, 1976. Experimental data correspond to  $x = 0.002$  ( $n = 3 \times 10^{19} \text{ cm}^{-3}$ ).  $C = C_{\text{exp}} \rho / n$ , where  $\rho = 2 \text{ g cm}^{-3}$ , is the single-particle specific heat.

#### 4. Absorption of ultrasound

Bayer and Sack (1968) detected evidence of cooperative effects in experiments with ultrasound. The effect of off-center ions on the scattering and absorption of sound is due to the interaction of the elastic moment of an off-center ion with the lattice distortions produced by the sound wave, which increases the elastic compliance of the crystal. At high temperatures, where no interaction between impurities shows up, the change  $\delta s / s$  in the elastic compliance is determined by the susceptibility of isolated elastic quadrupoles and, like the temperature dependence of the permittivity, should follow the relation  $\delta s / s \propto T^{-1}$ . Experiments have shown a departure from this relation to occur with decreasing temperature, the actual relation being approximately  $\delta s / s \propto (T + \theta)^{-1}$ . It follows that the interaction effect reduces not only the polarizability of electric dipoles coupled to off-center ions, but also the susceptibility associated with elastic dipoles. The  $\theta$  value is close to  $T_m$ , which indicates the governing role played by electric dipole-dipole forces in this phenomenon. This conclusion has been confirmed by numerical estimates (Bayer and Sack, 1968) which have shown the elastic interactions between off-center ions to be indeed of minor importance here.

#### 5. Thermal conductivity

The effect of off-center ions on the thermal conductivity is due to scattering of phonons by tunneling states. The maximum thermal resistance should therefore be observed when the energy of thermal phonons becomes comparable with the tunneling splitting energy. The dipole-dipole interaction shows up as an increase in tunneling energy due to the Stark effect, which is accompanied by an increase in the scattering cross section for higher-frequency phonons and shifts the thermal resistance maximum towards higher temperatures (Peressini *et al.*, 1969; Fiory, 1970).

Manifestations of electric dipole-dipole interactions between impurities have also been observed in some other experiments. In particular, Lüty (1967) has found a concentration dependence of the electro-optic and elasto-optic effects. Data on the concentration dependence of the infrared absorption coefficient have been reported by Barker and Sievers (1975).

#### B. Theoretical concepts

The experimental data presented above allow the following basic features of cooperative behavior of dipole impurity systems in weakly polarizable dielectric hosts to be identified: (1) Interaction effects reduce the polarizability of the system and produce no spontaneous polarization. (2) The presence of residual polarization and a logarithmic frequency dependence of the permittivity indicate that the low-temperature behavior of the system is

characterized by metastable states having very long relaxation times.

Let us now consider the physics of the observed phenomena.

### 1. Decrease in dielectric susceptibility due to dipole interaction

The fact that temperature  $T_m$  [Eq. (2.1)] is proportional to the mean dipole-dipole interaction energy is direct evidence that it is just this interaction that is dominating, although elastic interactions may also be substantial in some cases.

It has been shown (Mahan, 1967; Mahan and Mazo, 1968) that when interaction between electric dipoles in a polarizable medium is considered, the difference between the field acting on a dipole and the macroscopic electric field should be taken into account. As a result of this difference, the dipole-dipole interaction Hamiltonian

$$V_{dd} = \frac{1}{\epsilon_0} \sum_{ij} \frac{1}{r_{ij}^3} [\mathbf{d}_i^* \mathbf{d}_j^* - 3(\mathbf{n}_{ij} \mathbf{d}_i^*)(\mathbf{n}_{ij} \mathbf{d}_j^*)] \\ = - \sum_i l_i \mathbf{E}_i \quad (2.4)$$

contains the effective rather than the true dipole moments (we shall discuss this point in greater detail in Sec. IV);  $\mathbf{E}_i$  is the effective local field (in energy units) acting on the  $i$ th dipole from adjacent impurities;  $\mathbf{n} = \mathbf{r}/r$ ; and  $l_i$  is the unit vector indicating the dipole-moment direction,  $l_i = \mathbf{d}_i/d_i$ .

We shall hereafter neglect tunneling effects, considering all dipoles as classical ones. This, as a rule, is not a serious limitation, since cooperative effects manifest themselves only when the mean dipole-dipole interaction energy exceeds the tunneling energy. In fact, from the Hamiltonian of Eq. (2.4) with classical dipoles it follows (Lawless, 1966a) that at  $T > T_m$  the effective single-particle polarizability  $\chi$  becomes smaller than the polarizability of noninteracting particles  $n\chi_0$ . To explain this fact, we use the virial expansion and represent  $\chi$  as

$$\chi = n\chi_0 + n^2 \int d\mathbf{r} [\frac{1}{2}\chi_{12}(\mathbf{r}) - \chi_0], \quad (2.5)$$

where  $\chi_{12}$  is the polarizability of a pair of dipoles interacting in accordance with the Hamiltonian of Eq. (2.4). The integration in Eq. (2.5) allows for the spread in the mutual positions of interacting pairs and brings  $\chi$  to the form

$$\chi = n\chi_0(1 - B/T). \quad (2.6)$$

The value of the coefficient  $B$  depends on the number of possible directions of a dipole in the lattice. Thus, for orientations along the [100] direction,  $B \simeq 0.25d^2n/k\epsilon_0$ , which is somewhat smaller than the experimental value,  $B \simeq T_m$  [Eq. (2.1)]. Lawless (1966a) has shown that the agreement with experiment can be significantly improved by excluding from Eq. (2.5) the contribution of "frozen" pairs whose energy exceeds  $kT$ , although the necessity

for such an exclusion of close pairs was not clear from his study. Vugmeister and Stefanovich (1988a) demonstrated the exclusion of close pairs to be due to the fact that the dynamic rather than the static susceptibility is measured in experiments of the type conducted by Fiory (1970) and de Yoreo *et al.* (1984) (although the measurement frequencies are ultralow). The calculation of the second dynamic virial coefficient  $B(\omega)$ , carried out by Vugmeister and Stefanovich (1988a), yielded a value that indeed considerably exceeded that of the second static virial coefficient, the dependence of the second virial coefficient on the frequency of the applied field being logarithmic (see Sec. III C). The values of  $T_m$  calculated by Vugmeister and Stefanovich (1988a) are in agreement with experiment.

At  $T \rightarrow T_m$ , as can be seen from Eqs. (2.1) and (2.6) the virial series diverge and the pair approximation becomes invalid. Hence the conclusion, derived by means of pair approximation, that the system polarizability at  $T > T_m$  decreases due to the dipole-dipole interaction (which prevents the ferroelectric phase transition) cannot as yet serve as a convincing argument of the impossibility of a spontaneous polarization at  $T < T_m$  (elucidating this point calls for other approaches, which will be discussed below).

### 2. Residual polarizations

The pair approximation can, however, explain the existence of the residual polarization, whose appearance results from the fact that reorientation of every dipole in a pair is difficult since it requires surmounting an additional potential barrier produced by an adjacent dipole. The closer the dipoles are to one another, the higher the potential barrier, and hence the longer the relaxation time of the dipole moment of the pair.

Let us now estimate the magnitude of the residual polarization on the assumption that the dipoles can rotate freely (Fiory, 1970). In this case the minimum pair energy corresponds to two configurations in which the two dipoles are either parallel or antiparallel to the radius vector  $r$  that connects them. The mean frequency  $\bar{\nu}$  of reorientation of the total dipole moment of a pair is determined by the potential barrier  $W = d^{*2}/\epsilon_0 r^3$  separating the two minima:

$$\bar{\nu} = \nu e^{-W/kT}, \quad (2.7)$$

where  $\nu$  is the frequency of reorientation of isolated dipoles.

When the residual polarization is measured at the initial time, all the dipoles are aligned in the external electric field  $\mathcal{E}$  and their average dipole moment is  $d^*|\overline{\cos\theta}| = d^*/2$ , where  $\theta$  is the angle between  $\mathcal{E}$  and  $r$ , and the bar denotes spatial averaging. After the field has been turned off, most of the dipoles depolarize rapidly in a time  $1/\nu$ , but those dipoles with close neighbors will take much longer to depolarize, namely, a time  $1/\bar{\nu}$ ,

since the potential barrier has to be surmounted for a pair to depolarize. The spacing of the dipoles in a pair being random, the resultant residual polarization is given by

$$P_r = \frac{1}{2} n d^* \int n d\mathbf{r} e^{-\bar{v}(W)t}. \quad (2.8)$$

For long enough  $t$  in Eq. (2.8) we can approximate

$$\exp[-\bar{v}(W)t] \simeq \theta[W - T \ln(vt)],$$

(Ma, 1980), which greatly simplifies the integration and finally yields

$$\frac{P_r}{n d^*} = \frac{2\pi}{3} \frac{n d^{*2}}{\epsilon_0 k T \ln(vt)}. \quad (2.9)$$

Thus  $P_r \propto n^2$ , which agrees with experiment. However, Eq. (2.9) predicts an inverse logarithmic time dependence of  $P_r$ , while the experimental data shown in Fig. 5 give a better fit to the relation  $P_r \propto \text{const} - \ln(vt)$ . This difference can be attributed (Ma, 1980) to a more accurate integration in Eq. (2.8), which is to be performed at not too great  $t$ . Moreover, allowance for a discreteness of dipole orientations reduces the value of the numerical factor in Eq. (2.9); for example, at  $d \parallel [100]$  the factor is 0.4.

### 3. Dipole glass: Comparison with spin glasses

The presence of residual polarization clearly shows that at low temperatures the system is characterized by metastable states separated from one another by potential barriers. A minimum of the dipole-dipole interaction Hamiltonian of Eq. (2.4) with respect to possible directions of every dipole, i.e., a local minimum (Bray and Moore, 1981) occurs in the metastable states. The condition for this minimum yields

$$\mathbf{E}_i = \lambda_i \mathbf{d}_i, \quad (2.10)$$

where  $\lambda_i$  are the Lagrange factors corresponding to the conditional extremum of Eq. (2.4) at  $|d_i| = \text{const}$ . It can also be shown (Bray and Moore, 1981) that  $\lambda_i \geq 0$  for all  $i$ .

Consequently, in metastable states at  $T=0$ , every dipole is oriented parallel to its local field, i.e., the system is characterized by "frozen" configurations of dipole moments. At finite temperatures (but lower than characteristic heights of barriers between metastable states), the local field strength determines the average thermal value of the dipole moment. Due to this, the local-field distribution function  $f(E) = \overline{\delta(E - E_i)}$  is the basic characteristic of metastable states. (The overbar denotes averaging over impurity configurations. At  $T=0$ , thermal fluctuations of  $E_i$  may be neglected.)

Because of the variable-sign nature of the dipole-dipole interaction potential and the random spatial distribution of dipoles, local fields at the impurities have different directions, and therefore, at low temperatures and no external actions, dipoles are frozen in random orienta-

tions. Such a low-temperature state of dipole moments randomly oriented in internal fields is commonly referred to as a dipole glass state, by analogy with a spin-glass state, which features similar properties (Edwards and Anderson, 1975; Fischer, 1983; Binder and Young, 1986).

Note, however, that the term "spin glass" is not as yet narrowly defined in the literature. It is sometimes used to denote only a special "nonergodic" state for which the relaxation time tends to infinity when the specimen dimensions tend to infinity, in contrast to, say, ordinary glasses for which the relaxation time is a characteristic of the material. No experimental evidence of such nonergodicity originating in dipole glasses is available so far. In other words, there is so far no final answer to the question of whether the dipole glass state occurs in real physical systems as a thermodynamic equilibrium one or whether it differs from the paraelectric state only by the presence of long-time relaxation modes. Although in an experiment it is rather difficult to distinguish nonequilibrium freezing from a truly equilibrium phase transition (these phenomena differing in an experiment only by the degree of pronouncedness of characteristic anomalies), studies of nonlinear dielectric susceptibility in  $\text{KCl:OH}^-$  (Saint-Paul and Gilchrist, 1986) revealed no effects of a critical increase of the susceptibility at all (see below), in contrast to the situation in CuMn-type spin glasses, which obviously argues against an equilibrium phase transition to the dipole glass state.

Therefore, when speaking of an analogy between the dipole glass and the spin-glass state, we mean simply an analogy between systems of randomly distributed spins and dipoles, whose interaction potential can change its sign. Just such systems of spins are denoted by the term "spin glass" in most publications.

### 4. Absence of long-range order

Let us now discuss why disordered dipole systems exhibit no spontaneous polarization or long-range ferroelectric order. We assume that, as usual, the crystal is under conditions of a zero depolarizing field.<sup>1</sup> The absence of spontaneous polarization is in this case not obvious, since with all the dipoles coherently oriented in one and the same direction, the mean local field  $\bar{E}_i$  equal to the Lorentz field  $\bar{E}_i = (4\pi/3)(d^*n/\epsilon_0)$  in the system will be nonzero. With small configurational fluctuations of local fields, the presence of a nonzero mean field is known to result in the energetic favoring, at low temperatures, of a state with coherently aligned dipoles; this state may therefore arise spontaneously. It has, however, been shown (Aharony, 1978; Vugmeister, 1984a; Vugmeister and Stefanovich, 1987a, 1990) that configurational fluctuations in a disordered dipole system are substantial, so that states with a preferred orientation of dipole mo-

<sup>1</sup>For example, between the plates of a shorted capacitor.

ments are not energetically favored because they do not meet the condition of a local minimum of the Hamiltonian (Vugmeister, 1984a).

Following Vugmeister (1984a), we introduce a unit vector  $l(\mathbf{E})$  which indicates the direction of the dipole moment of an impurity in a local field  $\mathbf{E}$ . It follows from Eq. (2.10) that  $l(\mathbf{E}) = \mathbf{E}/E$  at  $T \rightarrow 0$ . If some preferred orientation of dipole moments exists in the system at low temperatures, then the value

$$L \equiv \bar{l} = \int d\mathbf{E} f(\mathbf{E}, L) l(\mathbf{E}) \quad (2.11)$$

will not be zero; the  $L$  value determines the relative number of coherently aligned dipoles and may be considered as a long-range order parameter. The solution of Eq. (2.11), the dependence of  $f(E)$  on  $L$  having been found beforehand, will answer the question of whether such a nonzero order parameter does exist in a dilute dipole system whose Hamiltonian is given by Eq. (2.4).

The function  $f(E)$  is readily calculated by neglecting the correlations between orientations of dipole moments and making use of the random-local-field approximation (for more detail, see Sec. III C and Appendix). When dipole moments have only two possible orientations, i.e.,  $l(E) = \pm 1$ , then

$$f(E) = \frac{1}{\pi} \frac{\delta}{(E - E_0 L)^2 + \delta^2}, \quad (2.12)$$

where  $\delta = 5.1nd^*/\epsilon_0$  is the half-width and  $E_0 = 3.5nd^*/\epsilon_0$  is the maximum most probable local field. Substitution of Eq. (2.12) in Eq. (2.11) shows that a solution with  $L \neq 0$  is possible only with  $(2E_0/\pi\delta) > 1$ , which cannot happen for the above values of  $E_0$  and  $\delta$ . A similar result is also valid for randomly oriented dipole moments.

Consequently, ferroelectric long-range order in dipole glasses with the dipole-dipole interaction Hamiltonian (2.4) is completely absent. This was first inferred by Aharony (1978), who considered the case of a continuously degenerate dipole system and analyzed its stability with respect to transverse fluctuations of the internal field. The above proof demonstrates (Vugmeister and Stefanovich, 1990) that, in a purely dipole system, long-range order is destroyed not only by transverse, but also by longitudinal fluctuations and is therefore equally applicable to discretely oriented dipole moments. Moreover, the above analysis shows that even a small change of the ratio between the  $E_0$  and  $\delta$  values would suffice for ferroelectric ordering to occur. The next section will show that just such a situation takes place in highly polarizable crystals.

## 5. Main properties of dipole glasses

Klein *et al.* (1976) described the thermodynamics of dipole glass at finite temperatures<sup>2</sup> in terms of the

<sup>2</sup>It is clear from the foregoing that only quasiequilibrium properties in metastable states have actually been dealt with.

random-mean-field approximation, which corresponds to replacement of  $E_i$  with  $\langle E_i \rangle$  in Eq. (2.4). This yields

$$f(E) = \overline{\delta(E - \langle E_i \rangle)}, \quad (2.13)$$

where  $\langle \dots \rangle$  is the thermal average. In contrast to the  $T=0$  case, not all the dipoles, but only those whose energy exceeds  $kT$ , are in this case frozen in local fields.

The relative number of frozen dipoles is

$$\mu(T) = |\overline{\langle l \rangle}|, \quad (2.14)$$

and this quantity may be considered as an order parameter of dipole glass (angle brackets denote a statistical averaging at a given local-field value). Klein *et al.* (1976) assumed *a priori* that  $L=0$ . The function  $f(E)$  found by them is a Lorentzian which is symmetric relative to  $E=0$  and whose width is  $\delta \propto \mu$ . Calculated values of  $\mu(T)$  are shown in Fig. 8, where an arrow indicates the temperature  $T_m$  corresponding to the permittivity maximum which is also presented by these authors.

In particular, it can be seen that about 80% of all the dipoles ( $\mu=0.8$ ) are completely frozen in local fields at  $T \approx T_m$ . With increasing temperature,  $\mu(T)$  decreases rapidly and becomes practically zero at  $T \approx 10T_m$ ; however, this function does not become strictly equal to zero at any temperature, since configurations were assumed to exist in which two dipoles could be spaced at an arbitrarily small distance from each other, and therefore closely spaced frozen pairs whose energy exceeds  $kT$  will be found for any temperature. Fischer and Klein (1976) attempted to consider a somewhat more realistic model by introducing a minimum possible finite spacing of dipoles. This model eliminates the nonphysical contribution of closely spaced pairs (whose spacing is less than the lattice constant) and predicts that above  $T_m$  the permittivity should exhibit a considerable cusp at the temperature  $T_g \propto n^{0.66}$ . At  $T > T_g$ ,  $\mu=0$ , and the behavior of  $\mu(T)$  is described by the Langevin-Debye law.

However, careful attempts (Potter and Anderson, 1981a, 1981b; de Yoreo *et al.*, 1984) to detect experimentally any cusp of  $\Delta\epsilon$  at  $T > T_m$  have proven unsuccessful. The absence of such a cusp appears to be due to the fact that pairs of dipoles whose spacings are on the order of

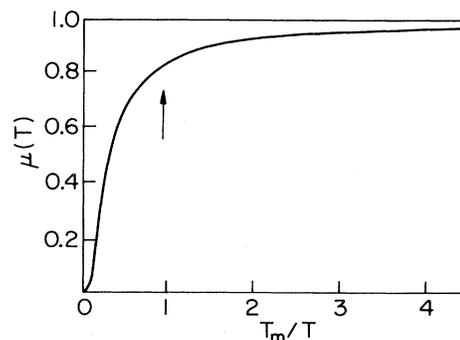


FIG. 8. Temperature dependence of dipole glass order parameter (Klein *et al.*, 1976).

the lattice constant are responsible for the singularity of  $\Delta\epsilon$  at  $T=T_g$ ; the possibility of describing such closely separated particles within the framework of the random mean-field approximation, neglecting the correlation effects, is very doubtful. Moreover, it is not at all clear to what extent a description in terms of the local-field distribution of Eq. (2.13) is applicable at high temperatures, since this equation ignores the thermal fluctuations of local fields.

It is obvious that, with an allowance for thermal fluctuations, the local-field distribution function should be represented as

$$f(E) = \overline{\delta(E - E_i)} \quad (2.15)$$

rather than by Eq. (2.13).

It can be shown, in particular, that, when we use Eq. (2.15), Eq. (2.11) is formally strictly valid, at least for the cases of two and eight possible orientations of dipole moments (Gallen, 1961; Thomsen *et al.*, 1984; Vugmeister and Stefanovich, 1988b). It is, however, clear that practical use of Eq. (2.15) calls for certain approximations. Vugmeister and Stefanovich (1987a) suggested that in calculating  $f(E)$  one neglects the correlations between orientations of dipole moments of different particles. In this case  $f(E)$  can be shown to assume at finite temperatures the same form as at  $T=0$ , i.e., the temperature dependence of  $f(E)$  is governed by the dependence  $L(T)$  alone and the dipole glass order parameter of Eq. (2.14) does not appear in the theory. Therefore, ignoring the correlations in Eq. (2.15), we lose the possibility of achieving a phase transition to the dipole glass state. However, as has already been noted, just such a point of view is substantiated by experiments with alkali halide crystals containing dipole impurities, since indications of an equilibrium phase transition to the dipole glass state were not observed in any experiment.

Figure 7 compares the specific-heat values for  $d\| [111]$ , calculated by Vugmeister and Stefanovich (1987b, 1989) using Eq. (2.15), with experimental values for KCl:OH<sup>-</sup> and the theoretical predictions of Klein *et al.* (1976). (Although, for OH<sup>-</sup>, the experimental values were for  $d\| [100]$  rather than  $[111]$ , this difference should not significantly affect the specific-heat behavior.) As can be seen from Fig. 7, the theory developed by Vugmeister and Stefanovich shows a fairly good qualitative agreement with the experimental data on the specific heat in classical dipole glasses, such as KCl:OH<sup>-</sup>, and describes the experiment much better than does the theory of Klein *et al.* (1976). Although, according to Klein *et al.*,  $C_v \propto T$  at  $T \rightarrow 0$ , the linear portion of the specific-heat curve presented by them is not reproduced within the experimental temperature range, the  $C_v$  dependence on  $T$  being weaker than linear. In contrast, the theory of Vugmeister and Stefanovich (1987b, 1989) reproduces a considerable linear portion of the specific-heat curve observed at 0.2 at. % OH<sup>-</sup>. Moreover, the high-temperature behavior of the specific heat presented by Klein *et al.* (1976) is seriously off, whereas the high-

temperature portion of the specific-heat curve calculated by Vugmeister and Stefanovich (1987b) is asymptotically exact as it follows from a comparison with a virial series. Note also that the linear low-temperature portion of the specific-heat curve in the random-field approximation stems from the fact that  $f(E)$  [Eq. (2.12)] tends to const at  $E \rightarrow 0$ . According to Baranovskii *et al.* (1980), who examined the part played by correlations at  $T \rightarrow 0$ , taking account of correlation effects for a dipole system results in only an insignificant change in the linear dependence of the specific heat, which turns into a  $T/|\ln T|^{1/2}$ -type dependence, as a consequence of the fact that  $(E) \rightarrow 0$  at  $E \rightarrow 0$ . Kirkpatrick and Varma (1978) conducted a numerical Monte Carlo modeling of  $f(E)$  at  $T=0$ , which confirmed that  $f(E)$  becomes zero at  $E=0$ , but they interpreted the derived dependence as  $f(E) \propto \sqrt{E}$ , which resulted in  $C \propto T^{3/2}$ . However, as Baranovskii *et al.* (1980) have asserted, the accuracy of the numerical experiment conducted by Kirkpatrick and Varma (1978) does not permit us to distinguish between  $T/|\ln T|^{1/2}$  and  $T^{3/2}$ .

In a recent paper Klein (1989) also took into account a tunneling splitting using a pair approximation.

We also note that isotropic correlations of length  $R_c \propto n^{-1/3}$  arise in KCl:OH<sup>-</sup> type dipole glasses at low temperature (Vugmeister and Stefanovich, 1989).

Vugmeister and Stefanovich (1988b, 1989), using the random-local-field method, calculated the nonlinear susceptibility of KCl:OH<sup>-</sup>, measured by Saint-Paul and Gilchrist (1986).

The dielectric susceptibility of dipoles can be accurately represented, to the terms quadratic with respect to the external electric field  $\mathcal{E}$ , as

$$\chi(\mathcal{E}) = \chi_1 - \chi_{nl} \mathcal{E}^2, \quad (2.16)$$

where  $\chi_1$  is the linear and  $\chi_{nl}$  the nonlinear susceptibility. A graph of the dependence  $\chi_{nl}(T)$  obtained by Vugmeister and Stefanovich (1988b) is shown in Fig. 9. As can be seen,  $\chi_{nl}(T)$  increases continuously with decreasing temperature. Figure 9 also shows experimental values of the susceptibility, calculated from the values of the coefficient  $a_3(T)$ , presented by Saint-Paul and Gilchrist (1988);<sup>3</sup> this coefficient, according to these authors, is determined by the relation

$$4\pi\chi_{nl} = \frac{9}{5} \frac{\epsilon_1^3(\epsilon_1 - \epsilon_0)a_3(T)}{(2\epsilon_1 + \epsilon_0)(2\epsilon_1^2 + \epsilon_0^2)(kT)^2}, \quad (2.17)$$

where

$$\epsilon_1 = \frac{1}{4}[(\epsilon_0 + \tau^{-1}) + \sqrt{(\tau^{-1} + \epsilon_0)^2 + 8\epsilon_0^2}];$$

$$\tau = \frac{k_B T}{nd^*2/\epsilon_0}.$$

<sup>3</sup>Curve 1b in Fig. 9.

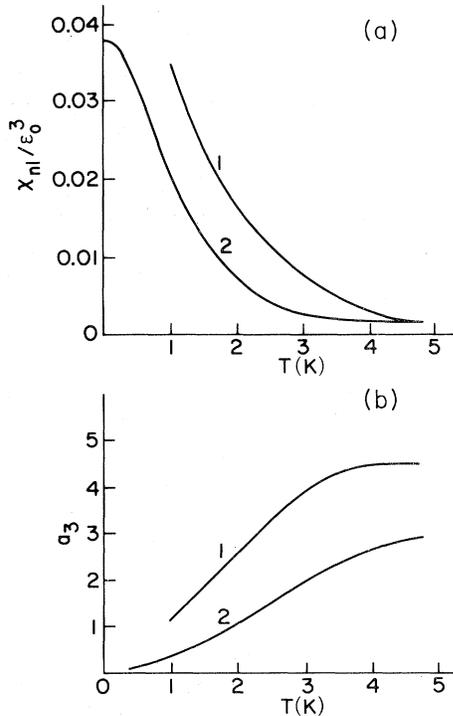


FIG. 9. (a) Temperature dependence of nonlinear dielectric susceptibility and (b) coefficient  $a_3$ . Curve 1, experimental results (Saint-Paul and Gilchrist, 1986); curve 2, theoretical predictions (Vugmeister and Stefanovich, 1988b).

Saint-Paul and Gilchrist (1986) demonstrated that Eqs. (2.17) separate out from the total susceptibility the effects of macroscopic dipole correlations, phenomenologically described by Onsager's reactive field. The coefficient  $a_3$  then takes into account only the correlations not described by the Onsager theory. Since the theory of Vugmeister and Stefanovich (1988b) requires no such artificial subdivision of the correlation effects, Eqs. (2.17) may be simply considered as the determination of the coefficient  $a_3$  and of its relation to  $\chi_{nl}$ .

It is essential to emphasize that in the case of a critical increase in nonlinear susceptibility the coefficient  $a_3$  should have increased with lowering temperature. The experiment, however, demonstrated the opposite behavior, in agreement with the theory of Vugmeister and Stefanovich (1988b), namely, a decrease in the coefficient  $a_3$  with lowering temperature. The same behavior was also observed for the coefficient  $a_5$ , which determines the nonlinear susceptibility of the fourth order.

From Fig. 9 it can be seen that the latter theory qualitatively describes the experimental results on the nonlinear susceptibility without the use of any fitting parameters (the value of the effective dipole moment of  $\text{OH}^-$ ,  $d^*$ , was measured from independent experiments). This evidence supports the adequacy of the proposed theory, based on the random-local-field method with allowance for the interaction potential of Eq. (2.4), to account for

the experimental situation.

Moreover, in our opinion, it is rather doubtful whether such systems can be described in terms of the cluster model with an antiferromagnetic interaction, proposed by Saint-Paul and Gilchrist (1986), where the number of particles effectively interacting in a cluster is independent of the temperature.

Vugmeister and Stefanovich (1988a) have described the effects of long-time relaxation in disordered dipole systems by combining the method of the random field and the method of clusters. They calculated the frequency-dependent dielectric susceptibility by using a dipole pair as the smallest structural unit interacting with the local field generated by the rest of dipoles. The theory described a logarithmic frequency dependence of the permittivity maximum observed for  $\text{KCl:OH}^-$ . The estimate of the temperature of the maximum, made by these authors, is in good accord with the experimental data.

Let us now briefly summarize the results presented in this section. We have tried to draw attention first of all to the fact that when off-center ions or other similar dipole impurities are introduced into weakly polarizable crystals, such as alkali halide crystals, the dipole-dipole interaction between the impurities brings about no ferroelectric ordering of dipoles. The low-temperature anomalies that arise, while in many aspects similar to those observed in CuMn-type spin glasses, nevertheless differ considerably in one important aspect, namely the absence of an equilibrium phase transition to the dipole glass state, which is most characteristically exhibited in experiments on the nonlinear susceptibility. The above-presented theoretical results have turned out to be capable of explaining why the dipole-dipole interaction does not result in the ferroelectric ordering of off-center ions. The question of why there is no equilibrium phase transition to the dipole glass state in such systems remains as yet unanswered.

Subsequent sections will consider distinguishing features of the cooperative behavior of off-center ions in highly polarizable crystals.

### III. POSSIBILITY OF FERROELECTRIC LONG-RANGE ORDERING IN HIGHLY POLARIZABLE CRYSTALS WITH OFF-CENTER IONS

#### A. Hamiltonian for dipole-dipole interaction

Studies of ordering in crystals containing off-center impurities acquired new impetus after Yacoby and Just discovered in 1974 that Li is an off-center ion when it substitutes for K in the highly polarizable dielectric  $\text{KTaO}_3$ , whose permittivity is two to three orders of magnitude greater than typical values for alkali halide crystals. The anomalies in the physical properties of  $\text{KTaO}_3\text{:Li}$ , which depend on the concentration of off-center ions, are pronounced at temperatures of  $T \sim 100$  K, while in alkali halide crystals they are appreciable

only at  $T \sim 1$  K. Although this fact is not unexpected and can be attributed to a great increase in the effective dipole moment  $d^*$  [which is evident, for example, from Eq. (2.1)], the question naturally arises whether there is a qualitative difference between the cooperative behavior of off-center ions in highly polarizable crystals and their behavior in classical dielectrics where the dipole glass state is attained. Such a difference may occur if the Hamiltonian for the interaction of dipoles in a highly polarizable dielectric does not reduce to the usual form of Eq. (2.4).

Let us therefore discuss in greater detail the basic assumptions making it possible to derive an explicit form of the interaction energy of impurity dipoles in a dielectric crystal. We shall see that highly polarizable hosts do indeed exhibit singularities stemming from spatial dispersion of permittivity, which is substantial in highly polarizable media. We shall present a derivation of the energy of interaction between dipoles in a highly polarizable dielectric medium, following Vugmeister and Glinchuk (1980).

Note first of all that an additional interaction between dipole impurities in a dielectric arises due to the fact that every one of the dipoles polarizes the lattice, and this dipole-induced polarization acts on adjacent impurities. The interaction of every dipole with the lattice polarization  $P(r)$  is accomplished by the field acting on the dipole, which is given by

$$\mathbf{E}_{\text{loc}}(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left[ \frac{4\pi}{3} \gamma \mathbf{P}_{\mathbf{q}} - 4\pi \frac{q}{q^2} (\mathbf{q} \cdot \mathbf{P}_{\mathbf{q}}) (1 - \delta_{\mathbf{q}0}) \right], \quad (3.1)$$

where  $\mathbf{P}_{\mathbf{q}}$  are Fourier components of the polarization. The second term in Eq. (3.1) corresponds to the macroscopic field (averaged over the unit cell). The Kronecker symbol  $\delta_{\mathbf{q}0}$  takes into account that the crystal is under conditions in which the macroscopic field is zero at a uniform polarization. The first term in Eq. (3.1) allows for the difference between the field acting on the dipole and the macroscopic field and is presented in the Lorentzian form that is valid for wave vectors  $q < a$  [ $a$  is the lattice constant (Born and Huang, 1954) and  $\gamma$  is the Lorentzian factor at the dipole location (for a purely ionic, simple cubic crystal,  $\gamma = 1$ )].

The validity of the first term in Eq. (3.1) implies that dipole impurities may be treated as point electric dipoles, i.e., the dipole size must be much smaller than the unit-cell size. Just this condition holds, in particular, for off-center ions. For definiteness, we shall consider slightly anharmonic crystals, whose high polarizability is due to the presence of soft phonon modes.

We represent the Hamiltonian for a system of  $N$  dipoles interacting with the lattice polarization as

$$H = - \sum_i \mathbf{d}_i \mathbf{E}_{\text{loc}}(r_i) + \sum_{qs} \hbar \omega_{qs} a_{qs}^\dagger a_{qs}, \quad (3.2)$$

where  $a_{qs}^\dagger, a_{qs}$  are operators of creation and annihilation of phonons of a frequency  $\omega_{qs}$  ( $s$  is the polarization in-

dex). In the case of multiatomic lattices, we shall confine ourselves in the sum over  $s$  in Eq. (3.2) to only one group of soft optical branches, threefold degenerate at  $q = 0$ , which are responsible for the anomalous value of permittivity  $\epsilon_0$ . At  $q \neq 0$ , this corresponds to taking into account two transverse ( $s_\perp$ ) and one longitudinal ( $s_\parallel$ ) branches.

Introducing, as usual, the normal coordinates

$$Q_{qs} = (\hbar/2\omega_{qs})^{1/2} (a_{qs}^\dagger + a_{qs}), \quad (3.3)$$

we represent  $P_{\mathbf{q}}$  as

$$P_{\mathbf{q}} = \frac{z^2}{(mN_0)^{1/2}v_0} \sum_s \epsilon_s^{-1} Q_{qs} \lambda_{qs}, \quad (3.4)$$

where  $z$  and  $m$  are, respectively, the effective charge and the mass of the oscillator;  $N_0$  is the number of unit cells of volume  $v_0$ ;  $\lambda_{qs}$  is the polarization unit vector;  $\epsilon_{s_\parallel} = \epsilon_\infty$  is the high-frequency permittivity;  $\epsilon_{s_\perp} = 1$ .

Using the equation of motion for the normal coordinates and the equilibrium condition  $\langle \dot{Q}_{qs} \rangle = 0$ , we determine the value of  $E_{\text{loc}}(r)$  for a fixed configuration of impurities (angle brackets denote the quantum-statistical averaging), and, as a result, obtain

$$E_{i\alpha\text{loc}}(r_i) = \sum_{jb} [\mathcal{H}_{1ij}^{\alpha\beta}(r_{ij}) + \mathcal{H}_{\parallel ij}^{\alpha\beta}(r_{ij})] \langle d_{jb} \rangle, \quad (3.5)$$

$$\begin{aligned} \mathcal{H}_{\perp}^{\alpha\beta}(r) = & - \frac{4\pi}{9V_0} \gamma^2 (\epsilon_0 - \epsilon_\infty) \sum_q \cos qr \frac{1}{1 + r_{c\perp}^2 q^2} \\ & \times \left[ \delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2} (1 - \delta_{\mathbf{q}0}) \right], \end{aligned} \quad (3.6)$$

and

$$\mathcal{H}_{\parallel}^{\alpha\beta}(r) = - \frac{4\pi}{9V_0} \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 \epsilon_\infty} (3 - \gamma)^2 \sum_{q \neq 0} \cos qr \frac{1}{1 + r_{c\parallel}^2 q^2} \frac{q_\alpha q_\beta}{q^2}, \quad (3.7)$$

where the well-known relation between the soft-mode frequency and the crystal permittivity,  $\epsilon_0 - \epsilon_\infty = 4\pi z^2 / m v_0 \omega_0^2$ , is used and the dispersion of oscillations is assumed to be (Born and Huang, 1954)

$$\begin{aligned} \omega_{q\perp}^2 &= \omega_0^2 + v_\perp^2 q^2, \quad \omega_{q\parallel}^2 = \omega_1^2 + v_\parallel^2 q^2, \\ \omega_1^2 &= \epsilon_0 \omega_0^2 / \epsilon_\infty, \quad r_{c\perp} = v_\perp / \omega_0, \quad r_{c\parallel} = v_\parallel / \omega_1. \end{aligned} \quad (3.8)$$

Here  $V_0 = N_0 v_0$  is the crystal volume, and  $\alpha, \beta$  are Cartesian coordinates.

In the sum over  $j$  in Eq. (3.5), the term with  $j = i$  should be discussed separately. This term represents the mean reactive field due to dipole-induced polarization, which acts on the dipole. Such a reactive field may lead to a "local phase transition" in a system of isolated dipoles in the lattice (Höck and Thomas, 1977; Höck *et al.*, 1979). The remaining terms in the sum in Eq. (3.5), i.e., those which will be considered further, represent a random field associated with indirect interac-

tion between dipoles through the field of optical phonons (the randomness being due to a random arrangement of impurities). According to Eq. (3.5), the Hamiltonian for such an indirect interaction has the form

$$V_{dd} = -\frac{1}{2} \sum_{ij, \alpha\beta} \mathcal{H}_{ij}^{\alpha\beta} d_i^\alpha d_j^\beta, \quad (3.9)$$

where  $\mathcal{H} = \mathcal{H}_\perp + \mathcal{H}_\parallel$ . Thus  $\mathcal{H}_\perp$  and  $\mathcal{H}_\parallel$  are constants of the indirect dipole-dipole interaction through the transverse and the longitudinal optical phonons, respectively.

Note that while  $r_{c\parallel} \lesssim a$  ( $a$  is the lattice constant), the value of  $r_{c\perp}$  is dependent on the value of the permittivity  $\epsilon_0$  and can greatly exceed  $a$  in highly polarizable crystals. However, for crystals with ordinary permittivity values (where  $r_c \lesssim a$  as well), considering dipole spacings of  $r > a$ , it may be assumed that  $r_c \simeq 0$  in Eqs. (3.6) and (3.7). Taking into account, along with Eqs. (3.6) and (3.7), the interaction between dipoles in a medium with permittivity  $\epsilon_\infty$  (at  $\epsilon_\infty = 1$  this corresponds to allowing for the interaction of dipoles in a vacuum), we arrive at the Hamiltonian of Eq. (2.4), where  $d^* = d [1 + \gamma(\epsilon_0 - 1)/3]$ . In highly polarizable crystals, however, the dipole-dipole interaction does not reduce to Eq. (2.4). Let us determine this interaction in an explicit form as a function of the dipole spacing.

From Eqs. (3.6) and (3.7) it follows that at  $\epsilon_0 \gg \epsilon_\infty$  the interaction between dipoles is predominantly through transverse phonons, and the contribution of longitudinal phonons can be neglected; we shall therefore consider  $\mathcal{H}_\perp$  alone. Extending the summation over wave vectors in Eq. (3.6) to infinity, which is possible at  $r > a$ , and proceeding to integration, we obtain

$$\begin{aligned} \mathcal{H}^{\alpha\beta}(r) &\simeq \mathcal{H}_\perp^{\alpha\beta}(r) \simeq (\gamma\epsilon_0/3) K^{\alpha\beta}(r); \quad (3.10) \\ K^{\alpha\beta}(r) &= \frac{1}{\epsilon_0} \left\{ \left[ \frac{2}{3} \frac{1}{rr_c^2} e^{-r/r_c} + \frac{4\pi}{3V_0} \right] \delta_{\alpha\beta} \right. \\ &\quad \left. + (3n_\alpha n_\beta - \delta_{\alpha\beta}) \right. \\ &\quad \left. \times \left[ \frac{1}{r^3} - e^{-r/r_c} \left( \frac{1}{r^3} + \frac{1}{r^2 r_c} + \frac{1}{r r_c^2} \right) \right] \right\}, \quad (3.11) \end{aligned}$$

where  $\mathbf{n} = \mathbf{r}/r$ ;  $r_c = r_{c\perp}$ .

The second term in Eq. (3.11) does not affect the interaction between dipoles spaced at finite distances, but allows for the boundary condition used in Eq. (3.1), i.e., that the mean macroscopic field in the specimen be zero. In this case every dipole is acted upon by an additional Lorentzian field from other impurities proportional to the mean dipole moment of the entire system.

Taking into account Eqs. (3.9)–(3.11), we can rewrite the Hamiltonian for the interaction of impurity dipoles in a highly polarizable crystal (at  $\epsilon_0 \gg \epsilon_\infty$ ) as

$$V_{dd} = -\frac{1}{2} \sum_{ij, \alpha\beta} K_{ij}^{\alpha\beta}(r_{ij}) d_{i\alpha}^* d_{j\beta}^* = - \sum_i \mathbf{I}_i \mathbf{E}_i, \quad (3.12)$$

where  $d^* = \gamma\epsilon_0 d/3$  is the effective dipole moment of the impurity in a highly polarizable crystal.

Note also that, as follows from the above, the specificity of a highly polarizable medium in the energy of interaction between impurity dipoles reflects the need to take into account the dispersion of the soft optical phonon. Because of the anomalously small value of the soft-mode frequency  $\omega_0$ , the dispersion of  $\omega_q$  shows up even at small  $q$  ( $q \sim r_c^{-1} < a^{-1}$ ), justifying the use of the long-wave approximation.

Note further that, since the crystal permittivity  $\epsilon_q \propto 1/\omega_q^2$ , the spatial dispersion of the permittivity may be believed to be responsible for the specificity of interaction between dipoles in a highly polarizable medium.

The Hamiltonian of Eqs. (3.11) and (3.12) is valid only for classical dipoles or if we neglect tunneling, which is possible at  $\Delta \ll \omega_0$  (where  $\Delta$  is the tunneling frequency), as otherwise the retarding effects will be significant [see, for example, Aminov and Kochelaev (1962)].

The Hamiltonian for the interaction of classical dipoles in a highly polarizable dielectric can also be derived in a different way, without explicit use of the soft-mode concept. For this purpose we note that the optical rigidity, associated with the transverse part of the polarization, is small in highly polarized crystals when the polarization is nonuniform throughout the specimen, and therefore, as has already been shown, it is the transverse polarization that makes the principal contribution to the magnitude of  $E_{\text{loc}}$  [Eq. (3.1)], so that only the first term need be left in this equation, i.e.,

$$E_{\text{loc}} = (4\pi/3)\gamma P(r), \quad (3.13)$$

since, if the polarization is transverse, then  $(\mathbf{q} \cdot \mathbf{P}_q) = 0$ , and the macroscopic field is zero.

The crystal energy associated with the transverse part of the polarization can be represented as

$$H_\perp = 2\pi V_0 \sum_q (\epsilon_0 - \epsilon_\infty)^{-1} P_{q\perp} P_{-q\perp}, \quad (3.14)$$

where  $P_{q\perp} = \hat{g} P_q$  and  $\hat{g}$  is the projection operator

$$g_{\alpha\beta} = \delta_{\alpha\beta} - q_\alpha q_\beta / q^2. \quad (3.15)$$

Using a long-wavelength approximation of  $\epsilon_q - \epsilon_0$  in the form

$$\frac{1}{\epsilon_q - \epsilon_0} = \frac{1}{\epsilon_0 - \epsilon_\infty} (1 + r_c^2 q^2), \quad (3.16)$$

and taking into account that  $\epsilon_0 \gg \epsilon_\infty$ , we represent the Hamiltonian for a system of dipoles interacting with the lattice of a highly polarizable dielectric as

$$H = -\frac{4\pi}{3} \gamma \sum_i \mathbf{d}_i \mathbf{P}(\mathbf{r}_i) + \frac{2\pi V_0}{\epsilon_0} \sum_q (1 + r_c^2 q^2) P_{q\perp} P_{-q\perp}. \quad (3.17)$$

Now, we determine from the condition  $\partial H / \partial P_{q\alpha} = 0$  the magnitude of the polarization  $P(r)$  induced by dipoles in the crystal. From Eq. (3.17) we obtain

$$P_\alpha(r_i) = + \frac{\epsilon_0}{4\pi} \sum_{j\beta} K_{ij}^{\alpha\beta}(r_{ij}) d_j^* , \quad (3.18)$$

and after substituting Eq. (3.18) into Eq. (3.17) we arrive again at the Hamiltonian for the dipole interaction in the form of Eq. (3.12).

The above-presented derivation, however, does not require the concept of long-lived phonons as elementary excitations of the crystal and is valid not only for a resonant, but also for a relaxational response of the lattice to an external perturbation. The only requirement is that there be a small value of the transverse optical rigidity (inverse permittivity) of a pure crystal.

Note also that, according to Eqs. (3.18) and (3.11), the total lattice polarization  $\int dr P(r)$  induced by an individual dipole in the crystal is equal to  $d^*$ , and therefore the  $d^*$  value may be regarded as the effective dipole moment of the impurity in the crystal. The change in the nature of the dipole field in a highly polarizable crystal can be attributed to the fact that the effective dipole moment can no longer be considered as a point dipole, since it has a finite characteristic size on the order of  $r_c$ . Only at  $r \gg r_c$  can the effective dipole size be neglected, and the usual expression for a dipole field in a dielectric becomes approximately valid.

Thus, in a highly polarizable crystal, the medium not only renormalizes the dipole moment of the impurity, but functionally changes the dipole-dipole interaction energy dependence on the spacing of dipoles.

### B. Suppression of local-field fluctuations and the possibility of a ferroelectric phase transition

The change in the dipole interaction potential in highly polarizable crystals leads to a number of important consequences. First of all, for impurity spacings  $r \lesssim r_c$ , the interaction fluctuations due to configurational fluctuations of particles are weakened because at  $r \lesssim r_c$  the function  $K(r)$  is smoother than  $r^{-3}$  [ $K(r) \propto r^{-1}$  at  $r \ll r_c$ ]. Moreover, as can be seen from Eq. (3.11), not only does the anisotropic part of the interaction, whose average (as in weakly polarizable crystals) is zero, change, but a new isotropic part appears which increases the most probable value of the local field acting on every dipole from adjacent impurities. Since with decreasing spacing of dipoles the isotropic part of the interaction increases while the interaction fluctuations diminish, it can be expected that at a high enough concentration of impurities, when the mean spacing becomes small enough,  $K(r)$  fluctuations may be neglected and the self-consistent mean-field approximation which predicts the existence of the ferroelectric phase transition will become valid.

Indeed, the phase-transition temperature  $T_c$  is determined by the appearance of a nonzero mean dipole moment

$$\overline{\langle d_{i\alpha}^* \rangle} = \overline{sp d_{i\alpha}^* e^{-\beta V_{dd}} / spe^{-\beta V_{dd}}} , \quad (3.19)$$

where the overbar denotes averaging over spatial configurations, and the angle brackets statistical averaging over orientations of dipole moments. Near  $T_c$ , as usual, the right-hand side of Eq. (3.19) can be expanded into a series in terms of  $V_{dd}$ , which yields

$$\overline{\langle d_{i\alpha}^* \rangle} = + \frac{d^{*2}}{3k_B T} \sum_{j\beta} \overline{K_{ij}^{\alpha\beta} \langle d_{j\beta}^* \rangle} . \quad (3.20)$$

Because of the random arrangement of impurities, the configurational average in Eq. (3.20) can be replaced by a product of averages,

$$\overline{\sum_{j\beta} K_{ij}^{\alpha\beta} \langle d_{j\beta}^* \rangle} \rightarrow \sum_{j\beta} \overline{K_{ij}^{\alpha\beta}} \overline{\langle d_{j\beta}^* \rangle}$$

only neglecting the fluctuations, which corresponds to the introduction of the mean field. The applicability of the mean-field approximation can be roughly estimated from the condition

$$\left[ \overline{\sum_{j\beta} K_{ij}^{\alpha\beta}} \right]^2 \gg \sum_{j\beta} \overline{(K_{ij}^{\alpha\beta})^2} , \quad (3.21)$$

which qualitatively reflects the small value of interaction fluctuations. Using the explicit form of  $K(r)$  from Eq. (3.21), we obtain a qualitative estimate of the applicability of the mean-field approximation beyond the critical region as

$$12\pi n r_c^3 \gg 1 . \quad (3.22)$$

Using the mean-field approximation, we obtain from Eq. (3.20) the temperature of the ferroelectric phase transition in a system of dipole impurities,

$$T_c = \frac{4\pi}{3} \frac{d^{*2} n}{k_B \epsilon_0(T_c)} = \frac{4\pi}{27k_B} \gamma^2 d^2 n \epsilon_0(T_c) . \quad (3.23)$$

Since  $\epsilon_0$  in highly polarizable crystals is a function of temperature, Eq. (3.23) is in fact an equation in  $T_c$ . If, for example, we approximate  $\epsilon_0(T)$  by the Curie-Weiss law,  $\epsilon_0(T) \propto (T - T_0)^{-1}$ , then, at  $T_c \gg T_0$ , Eq. (3.23) yields

$$T_c \propto \sqrt{n} .$$

Simultaneously with the ordering of dipoles, a spontaneous polarization of the lattice appears because of the existing linear relation between the average dipole moment of the impurities and the lattice polarization. Indeed, it follows from Eq. (3.18) that

$$\langle \bar{\mathbf{P}} \rangle = n \langle \bar{\mathbf{d}}^* \rangle . \quad (3.24)$$

This means that at a high enough concentration the dipole impurities induce in a highly polarizable crystal a ferroelectric phase transition.

The above rough estimate, however, gives no indication as to what impurity concentrations suffice for the ferroelectric phase transition to occur. This point will be discussed in more detail in the next section.

### C. Concentrational ferroelectric phase transition. Random-field theory

As has been shown above, in highly polarizable crystals the conditions under which the mean-field approximation is valid are more likely to occur at a high concentration of dipoles. The ferroelectric phase-transition temperature has been estimated in the mean-field approximation. However, the domain of applicability of these results remains unclear unless we can find an approach enabling us to go beyond the framework of the mean-field theory.

The simplest and most natural generalization of the mean-field method in disordered systems is the so-called random-field method, where, as in the mean-field one, the correlation between dipoles is neglected, but the randomness of the field acting on every dipole from its adjacent impurities is taken into account. As a result, the local-field distribution function

$$f(E) = \overline{\delta(E - E_i)} \quad (3.25)$$

[where  $E_i$  is determined by Eq. (3.12)], which in the Weiss mean-field approximation is

$$f(E) = \delta(E - \overline{E_i}), \quad (3.26)$$

is replaced in the random-field approximation by a smooth function of finite width, determined in a self-consistent manner. We shall show (Vugmeister, 1984) that the random-field approximation allows us to understand clearly why a ferroelectric phase transition is impossible in dilute dipole systems operating under the usual law of the dipole-dipole interaction; the random-field approximation, moreover, allows us to estimate the critical concentration at which ferroelectric long-range ordering "originates" at  $T=0$  in highly polarizable crystals containing dipole impurities, i.e., when a concentrational phase transition occurs.

Consider a system of dipole impurities, randomly distributed in a crystal, at temperatures much lower than the characteristic interaction energy for dipoles spaced at average distances from one another. At such low temperatures the orientation of every dipole may be considered parallel to the local field acting on it from adjacent impurities (we neglect tunneling effects). Although such states, as has already been noted, are not fully in equilibrium, being metastable with respect to simultaneous reorientations of many dipoles while the total dipole moment of the system remains unchanged, they can be approximately treated as equilibrium states for times shorter than their relaxation times, which are rather long.

Due to the varying sign of the interaction potential [Eqs. (3.11) and (3.12)], the local fields acting on every impurity may have various directions, and therefore at low temperatures the dipoles are generally frozen in random orientations.

The task is to find out in what cases such a random distribution of dipole orientations is fully chaotic, so that

the dipole moment of the whole system, averaged over configurations of the particles, is zero and, conversely, under what conditions a nonzero average dipole moment can appear.

To answer this question, we resort to the random-field method. The essence of the random-field approximation is as follows. First, we change Eq. (3.25) to an integral representation, assuming

$$f(\mathbf{E}) = \frac{1}{(2\pi)^3} \int d\rho e^{i\rho\mathbf{E}} e^{-F(\rho)}, \quad (3.27)$$

$$e^{-F(\rho)} = e^{-i \sum_j \rho_\alpha J_{ij}^{\alpha\beta} l_{j\beta}}, \quad (3.28)$$

where  $J_{ij}^{\alpha\beta} = d^* K_{ij}^{\alpha\beta}$  has been introduced for convenience.

The explicit form of the function  $F(\rho)$  is very difficult to find because of correlations between orientations of the dipole moments of different particles. The problem is greatly simplified if we neglect the correlations and consider the quantities  $l_i$  as independent random variables. In this case  $F(\rho)$  converts to the form

$$F(\rho) = n \int d\mathbf{r} \int dl \varphi(l) (1 - e^{i\rho \hat{\mathbf{r}} \cdot l}), \quad (3.29)$$

where the thermodynamic limit  $N \rightarrow \infty$ ,  $V_0 \rightarrow \infty$ ,  $n = N/V_0 = \text{const}$  is used and  $\varphi(l)$  is the distribution function of the dipole moments in the orientations,

$$F(\rho) = F_1(\rho) - iF_2(\rho).$$

The real part of the function  $F(\rho)$ , i.e.,  $F_1$ , describes the spread of local fields in a disordered dipole system, which prevents ferroelectric ordering of the dipoles, while the imaginary part  $F_2$  determines the most probable magnitude of the local field that tends to orient the dipoles coherently.

If some preferred orientation of dipole moments exists in the system at low temperatures, then the relative number of coherently oriented dipoles is given by Eq. (2.11), which determines the value of the order parameter  $L$ . If the dipoles can be oriented in only two possible directions, Eq. (2.11) transforms to

$$L = \frac{2}{\pi} \int d\rho e^{-F_1(\rho)} \frac{\sin[E_0(\rho)\rho L]}{\rho}, \quad (3.30)$$

where

$$F_1(\rho) = n \int d\mathbf{r} [1 - \cos \rho J^{zz}(\rho)], \quad (3.31)$$

$$E_0(\rho) = -\frac{F_2(\rho)}{\rho L} = \frac{n}{\rho} \int d\mathbf{r} \sin \rho J^{zz}(\rho). \quad (3.32)$$

The problem thus consists in finding out the conditions under which this system has a solution with  $L \neq 0$ .

Equations (3.30)–(3.32) with  $K^{\alpha\beta}(r)$  in the form of Eq. (3.11) have been numerically solved (Vugmeister, 1984; Vugmeister and Stefanovich, 1987a) for various values of the parameters  $nr_c^3$ ; the results are shown in Fig. 10. This figure shows that at some critical concentration ferroelectric ordering occurs, i.e., a solution with a nonzero average dipole moment appears.

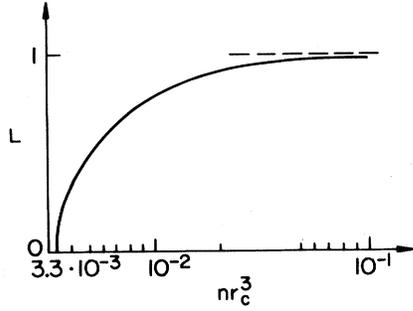


FIG. 10. Ferroelectric long-range order parameter as a function of  $nr_c^3$  (Vugmeister, 1984).

Thus it may be asserted that a concentrational ferroelectric phase transition is brought about in highly polarizable crystals by increasing the dipole impurity concentration at low temperatures ( $T \rightarrow 0$ ). The critical concentration for such a phase transition corresponds to the condition (Vugmeister and Stefanovich, 1987a)

$$n_{cr} r_c^3 \approx 0.3 \times 10^{-2}. \tag{3.33}$$

It may also be seen that within the range  $0.3 \times 10^{-2} < nr_c^3 < 10^{-1}$  the order-parameter value differs from  $L=1$ , which corresponds to a parallel orientation of all the dipole moments. This means that over this concentration region the spread of orientations of dipole moments of different impurities is substantial, and there can be no approximation of a mean field that is the same for every point of the crystal. The mean-field theory is applicable only at  $nr_c^3 \gtrsim 10^{-1}$ , where, as can be seen from the figure, the difference of  $L$  from unity may be neglected, whereas near the critical concentration the solution of Eq. (3.30) yields

$$L \propto (n - n_{cr})^{1/2}, \quad n \rightarrow n_{cr}. \tag{3.34}$$

The value of the critical exponent in Eq. (3.34) is closely connected to the random-field approximation. In close proximity to  $n_{cr}$  this approximation is obviously inadequate, as correlation effects should show up here. At the same time, the estimate of the critical concentration value, obtained by us by use of the random-field method, should be qualitatively correct (see Appendix).

From the above analysis it also follows that there is no long-range order in the case of an ordinary dipole-dipole interaction potential. Note that this conclusion, which we obtained for the case of dipoles with discrete possible orientations, is quite different from the proof by Aharony (1978) for a continuously degenerate dipole system, based on its instability with respect to transverse fluctuations of the internal field. From our analysis it follows that in a purely dipole system,  $J^{\alpha\beta} \propto r^{-3}(\delta_{\alpha\beta} - 3n_\alpha n_\beta)$ , long-range order is destroyed not only by transverse, but also by longitudinal fluctuations.

To generalize the random-local-field method for the case of finite temperatures, it should be assumed in Eq.

(2.11) that

$$l(E) = \tanh \beta E, \tag{3.35}$$

which results in the following expression for the ferroelectric long-range order parameter:

$$L = \int \frac{\sin[\rho E_0(\rho)L] e^{-F_1(\rho)} d\rho}{\sinh(\pi \rho k_B T/2)}. \tag{3.36}$$

For  $T_c$  we obtain from Eq. (3.36) (with  $L \rightarrow 0$ )

$$\frac{1}{k_B T_c} = \int \frac{\rho E_0(\rho) e^{-F_1(\rho)} d\rho}{\sinh(\pi \rho k_B T_c/2)}. \tag{3.37}$$

If we substitute for the functions  $F_1(\rho)$  and  $E_0(\rho)$  in Eq. (3.36) their values as  $\rho \rightarrow 0$ , i.e., if we assume  $F_1(\rho) \rightarrow 0$ ,  $E_0(\rho) \rightarrow E_0$ , then

$$E_0 = \lim_{\rho \rightarrow 0} E_0(\rho) = n \int dr J^{zz}(e),$$

and the well-known equation of the Weiss mean-field theory results,

$$L = \tanh(LE_0/k_B T), \text{ i.e., } k_B T_c^{\text{MF}} = E_0,$$

where  $T_c^{\text{MF}}$  is the phase-transition temperature in the mean-field approximation. This limit is, however, attained only with a very high concentration of impurities, while in the more general case the dependence of the functions  $E_0$  and  $F_1$  on  $\rho$  is quite substantial.

Assuming  $T_c \rightarrow 0$  in Eq. (3.37), we obtain an equation determining the critical concentration of dipoles, below which a ferroelectric phase transition does not take place,

$$\frac{2}{\pi} \int_0^\infty E_0(\rho) e^{-F_1(\rho)} d\rho = 1. \tag{3.38}$$

Note that Eq. (3.38) can be derived directly from Eq. (3.30), assuming  $L \rightarrow 0$ . Equation (3.38) leads to the condition presented by Eq. (3.33).

Substituting the explicit form of the potential into Eq. (3.37) yields (Vugmeister and Stefanovich, 1987a) the ferroelectric phase-transition temperature as a function of  $nr_c^3$ . The authors have obtained the  $T_c(nr_c^3)$  dependence for eight possible dipole orientations, as shown in Fig. 11, where the critical concentration is  $n_{cr} = 4.65 \times 10^{-3} r_c^{-3}$ .

#### D. Long-time relaxation effects

We have shown above that the simple random-local-field theory gives a qualitatively correct description of the main equilibrium properties of disordered dipole systems. However, an attempt to extend these simple concepts to account for dynamic effects entails additional difficulties. Vugmeister and Stefanovich (1988a) have shown that application of the random-local-field theory to dynamic effects preserves the nature of the relaxation unchanged, i.e., retains the single exponent, while reducing the effect of dipole interaction merely to a change in the single-particle relaxation rate  $\nu$ ,

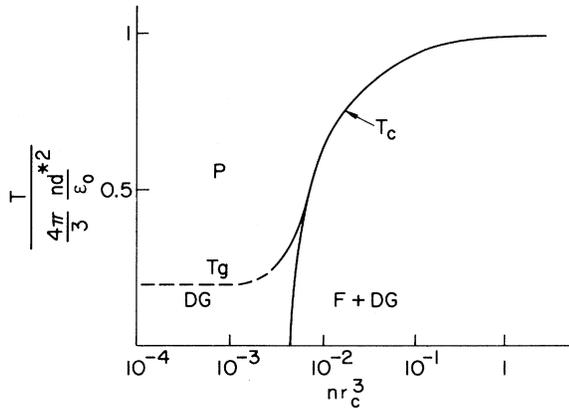


FIG. 11. Phase diagram of the random dipole system ( $d_{\parallel}/111/\nu$ ) with Hamiltonian (3.11): *P*, paraelectric phase; *DG*, metastable dipole glass [ $T_g \equiv T_g(\omega/\nu=10^{-8})$ ] with no long-range order, *F+DG*, mixed phase with coexisting ferroelectric and dipole glass properties. From Vugmeister and Stefanovich, 1987a, 1988a.

$$\bar{\nu} = \nu \left[ 1 - \int dE l(E) E \left[ \frac{\partial f(E, L)}{\partial L} \right]_{L=0} \right], \quad T > T_c. \quad (3.39)$$

Since the expression in square brackets goes to zero at  $T = T_c$ , Eq. (3.39) describes the critical slowing down of the relaxation, associated with the presence of a phase transition. Moreover, according to Eq. (3.39), the slowing down of the relaxation occurs only in a narrow region near  $T_c$ . Such a slowing down is the single source of long-term relaxation in ordered systems [as well as in disordered systems at  $nr_c^3 \gg 1$ , when the mean-field ap-

proximation is valid and  $\bar{\nu} = \nu(1 - T_c/T)$ ].

In disordered systems, however, at  $nr_c^3 < 1$  there is an additional long-time relaxation mechanism, associated with the presence of closely spaced particle clusters. The relaxation of such clusters is impeded because the interaction of dipoles in a cluster gives rise to additional potential barriers, which impede the reorientation of the dipoles. As noted in Sec. II B, it is just such a mechanism that is responsible for the long-time relaxation in dipole glasses. Because of the random spacing of dipoles in clusters, a distribution of relaxation times takes place, which results in the observed nonexponential relaxation of the system.

The existence of long-time nonexponential relaxation in a dipole system can be ascertained by a virial expansion of the dynamic susceptibility (Vugmeister and Stefanovich, 1988a).

The dynamic susceptibility  $\chi(\omega)$  can be, accurately to the second virial coefficient, represented as (Vugmeister and Stefanovich, 1988a)

$$\chi(\omega) = \chi_0(\omega) \left[ 1 + \frac{B(d^{*2}/k_B T \epsilon_0 r_c^3, \omega/\nu)}{T} + \frac{4\pi}{3} \frac{nd^{*2}}{k_B T \epsilon_0} \frac{1 - \omega^2/\nu^2}{1 + \omega^2/\nu^2} \right]. \quad (3.40)$$

The third term in Eq. (3.40) represents the contribution of the Lorentzian field, i.e., this equation describes the response to the mean macroscopic rather than the local field [see also Vugmeister and Stefanovich (1985), who used such a procedure when calculating the second virial coefficient of the static susceptibility].

At  $\omega/\nu \ll 1$  the function  $B(d^{*2}/k_B T \epsilon_0 r_c^3, \omega/\nu)$  has the following asymptotic representations:

$$B \left[ \frac{d^{*2}}{k_B T \epsilon_0 r_c^3}, \frac{\omega}{\nu} \right] = \frac{nd^{*2}}{k_B \epsilon_0} \begin{cases} \frac{8\pi}{3} \frac{\nu^2 - \omega^2}{\nu^2 + \omega^2}, \quad \frac{nd^{*2}}{k_B T \epsilon_0 r_c^3} \gg 1, & (3.41a) \\ -\frac{4\pi}{3} \left[ 0.16 + \frac{8}{3\sqrt{3} \ln[(2\nu - \omega)/\omega]} \right], \quad \frac{nd^{*3}}{k_B T \epsilon_0 r_c^3} \ll 1, \quad \omega/\nu \ll 1. & (3.41b) \end{cases}$$

Equation (3.41a) describes the high-temperature behavior of the dynamic susceptibility in the mean-field approximation. From the equation it follows that within the domain of applicability of the mean-field approximation the frequency dispersion of the second virial coefficient is determined solely by the frequency scale of reorientation of isolated dipoles (the relaxation is single exponential), and at  $\omega/\nu \ll 1$  there is no frequency dispersion of *B*.

A different situation occurs at the opposite limit [Eq. (3.41b)], which corresponds to the case of weakly polarizable dielectrics with the usual law of interaction between dipoles [i.e., if  $r_c \rightarrow 0$  is assumed in Eq. (3.11)]. Equation (3.41b) describes the logarithmic frequency dependence of the second virial coefficient, which has already been discussed in Sec. II B. The numerical value of the dy-

amic virial coefficient substantially exceeds that of the static coefficient.

For highly polarizable crystals the dispersion of the second virial coefficient is generally governed<sup>4</sup> by the value of the parameter  $\xi = d^{*2}/k_B T \epsilon_0 r_c^3$ . It should be noted here that the two limits, Eqs. (3.41a) and (3.41b), are not equivalent. The former can always be attained by increasing the temperature, while the possibility of attaining the latter is determined by the applicability of the virial expansion, requiring the sum of the second and

<sup>4</sup>The contribution of closely spaced pairs to the long-term relaxation decreases with increasing parameter  $nr_c^3$ .

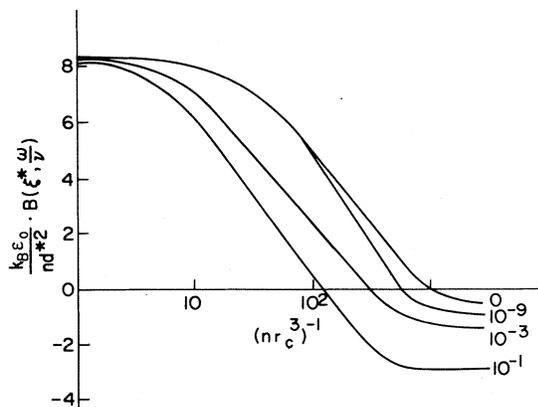


FIG. 12. Dynamic second virial coefficient as a function of  $nr_c^3$  for different values of parameter  $\omega/\nu$ . From Vugmeister and Stefanovich, 1988a).

third terms in Eq. (3.40) to be less than unity. This means that the permissible range of temperatures and hence also the range of values of the parameter  $\xi$  are limited by the condition  $\xi < \xi^*$ , where the value of  $\xi^*$  is determined from the condition of equating of the sum of the second and third terms in Eq. (3.40) to unity. Figure 12 shows the dependence  $B(\xi^*, \omega/\nu)$  as a function of  $nr_c^3$ . As can be seen, the frequency dispersion of  $B(\xi^*, \omega/\nu)$  at  $\omega/\nu \ll 1$  is appreciable right up to values of  $nr_c^3 \lesssim 0.1$ , at which the mean self-consistent field theory is already applicable with adequate accuracy to describe the equilibrium properties of the system under consideration,<sup>5</sup> i.e., dynamic effects are more sensitive to spatial disorder in the arrangement of particles than are equilibrium properties.

Vugmeister and Stefanovich (1988a) have shown that the concept of slowly relaxing dipole clusters (in particular, pairs) that are responsible for a low-frequency dispersion of the dielectric response can also be useful in analyzing the susceptibility at low temperatures; this is so despite the fact that the virial expansion in this temperature range is inapplicable, since at low temperatures the interaction is substantial not only between particles in clusters, but also between different clusters. These authors suggested that both the interaction between dipoles in a cluster and the interaction between clusters be taken into account by introducing a random local field acting on every dipole in a cluster from dipoles belonging to other clusters. This implies a generalization of the random-local-field theory for describing the clusters. Note that the approach proposed by these authors, while resembling the usual Bethe-Peierls cluster method (see,

<sup>5</sup>The condition  $B(\xi^*)=0$  indicates roughly the occurrence of a ferroelectric phase transition (Vugmeister and Stefanovich, 1985).

for example, Vaks, 1973), is not fully equivalent to the latter in that the interaction between clusters is effected through the random field rather than through the mean field used by Bethe and Peierls.

Vugmeister and Stefanovich (1988a) calculated the frequency-dependent maximum temperature of dielectric susceptibility for  $n \ll n_{cr}$  to be

$$T_m \simeq -15nd^2/\epsilon_0 \ln(\omega/\nu).$$

The similarity between  $T_m$  and the frequency-dependent dipole glass transition temperatures  $T_g$  is obvious. Such a dipole glass state is a nonequilibrium metastable state, as was discussed in Sec. II.

Figure 11 shows the phase diagram of a random-site dipole system taking into account the obtained values of  $T_c$  and  $T_g$ . The approach (1988a) of Vugmeister and Stefanovich also predicts that in the narrow region of dipole concentration at  $n \gtrsim n_{cr}$  (but  $T_c < T_g$ ) the frequency-dependent susceptibility will develop two maxima. The broad high-temperature maximum is connected with the freezing of close pairs, whereas the low-temperature maximum comes from a long-range-order phase transition.

#### IV. COEXISTENCE OF FERROELECTRIC AND DIPOLE GLASS PROPERTIES IN HIGHLY POLARIZABLE CRYSTALS CONTAINING DIPOLE IMPURITIES (KTaO<sub>3</sub>:Li, Na, Nb)

The preceding section presented a qualitative picture of the phenomena to be expected in highly polarizable crystals containing dipole impurities. As will be shown below, although the experimental situation is much more complex, the principal theoretical inference, namely, that new properties stemming from the change in the dipole-dipole interaction potential arise in highly polarizable crystals containing dipole impurities, is nevertheless in agreement with experiments.

The number of experimental studies of the cooperative behavior of dipole impurities is at present much greater for highly polarizable crystals than for alkali halide crystals, described in Sec. II A. These systems have been studied by dielectric, optical, x-ray, NMR, EPR, acoustic, and other techniques. The large number of studies is a result of the fact that such substances exhibit under certain conditions both ferroelectric and dipole-glass properties. As a result of inadequate understanding of such behavior, various researchers expended much effort in attempting to prove that one or another of these crystals were either ordinary ferroelectrics or close to traditional dipole glasses, such as KCl:Li<sup>+</sup>. Scientists even divided into groups advocating one or the other opinion. It has, however, become clear by now that such a discussion, which lasted over a decade, was mainly due to the need to expand the current terminology, since the observed anomalies in highly polarizable crystals containing dipole impurities are incompatible with both traditional

dipole glasses, such as  $\text{KCl}:\text{OH}^-$ ,  $\text{Li}^+$ , and ordinary ferroelectrics, such as  $\text{BaTiO}_3$  and  $\text{KH}_2\text{PO}_4$ .

Practically all workers in this field now recognize the existence in  $\text{KTaO}_3:\text{Li}$ , Na, and Nb crystals of large macroscopic polar regions with a length scale at least  $1000\text{--}10\,000\text{ \AA}$ , where the polarization is approximately uniform. This situation differs substantially from that in traditional dipole glasses, where the short-range order extends over a much smaller scale. At the same time, because the uniform polarization regions are small compared with the sizes of domains in ordinary ferroelectrics and because long-time relaxation effects occur in impurity systems due to spatial disorder, as was shown in Sec. III D, some phenomena are similar to those observed in dipole glasses.

Before presenting below a description and analysis of experimental results, we wish to emphasize once again that, although the body of experimental work is much richer and much more complex than the simple physical notions described in the theoretical part of this review, and many details of the experiments still call for a deeper theoretical interpretation, the principal theoretical conclusion is beyond doubt: that introduction of dipole impurities into a highly polarizable crystal (provided that a corresponding criterion is met) induces ferroelectric domains, i.e., macroscopic spontaneous polarization regions.

Let us now look at the experimental data.

#### A. $\text{KTaO}_3:\text{Li}$ (KTL)

The situation in  $\text{KTaO}_3:\text{Li}$  will be discussed in the greatest detail since, first, the off-center position of Li has been reliably established, allowing it to be classed with confidence as having dipole impurities, and, second, the physical phenomena are fairly well understood for this crystal.

The off-center position of Li in potassium tantalate was first discovered in Raman experiments (Yacoby and Just, 1974), where a first-order scattering peak was observed, ascribed to a resonance impurity mode induced by the off-center Li. Subsequent high-precision measurements (Prater *et al.*, 1981a, 1981b) of Raman spectra demonstrated, however, that although the conclusion (Yacoby and Just, 1974; Yacoby *et al.*, 1977) of the off-center position of Li was correct, the observed scattering peaks were due not to a resonance mode (only peak B in Fig. 13 is due to such a mode), but to the action of quasistatic fields of lithium dipoles, which change the selection rules and permit first-order scattering by lattice modes to be observed. Figure 13 shows that the intensity of the first-order scattering by acoustic and optical vibration branches increases with increasing Li concentration (peaks A,  $\text{TO}_2$ ). However, the first-order peaks are distinct even for nominally pure specimens, indicating the presence of extraneous impurities.

The off-center position of Li is borne out by dielectric, NMR, and EPR studies. Measurements by Höchli *et al.*

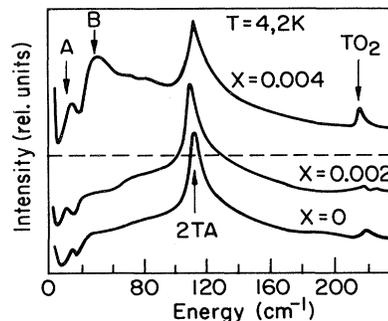


FIG. 13. Raman spectra of  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$  (Prater *et al.*, 1981a). Peaks A and B are due to first-order scattering by acoustic and soft optical vibrations, respectively.

(1978, 1979) of the frequency dependence of the permittivity of KTL have shown that the presence of Li leads to a low-frequency dispersion of  $\epsilon$ . This indicates a relaxational behavior of reorientations of impurities between different off-center positions. The reorientation frequency follows the Arrhenius law

$$\nu = \nu_0 e^{-U/T}, \quad (4.1)$$

with  $\nu_0 \approx 1.6 \times 10^{13} \text{ s}^{-1}$  and  $U = 1000 \text{ K}$ . As a result of such a high barrier, characteristic reorientation times exceed tens of second, which is much longer than the experimentally attainable observation times, and hence the low-temperature dynamics of Li turns out to be frozen in experiments. This freezing, however, is of a single-particle nature, i.e., it occurs at arbitrarily low concentrations of Li, and should not be confused with the cooperative effects discussed in Sec. III D. Because of the single-particle character of the thermal freezing of the off-center ions, the residual polarization at low Li concentrations should be a linear function of  $n$ , and this has been indeed been observed experimentally. Based on measurements of the residual polarization at various orientations of the external electric field, Höchli *et al.* (1979) have shown the off-center displacement of Li to be along the  $[100]$  direction.

This was subsequently confirmed by analysis (Borsa *et al.*, 1980; van der Klink *et al.*, 1983) of the quadrupole splitting of  $\text{Li}^+$  NMR lines. The quadrupole structure appears in the spectrum because of the interaction between the quadrupole moment of the nucleus of the off-center ion and the gradient of the intercrystalline electric field. Since in a cubic crystal the electric-field gradient is zero at the centrally-symmetric site of the unit cell (which follows from the Laplace equation), the appearance of quadrupole splitting unambiguously reveals the off-center positions of the ion. The direction of the off-center displacement, which lies in the axis of the electric-field gradient, is determined from the dependence of the number and position of quadrupole satellites on the magnetic-field orientation. Measurements of the quadrupole splitting  $\nu_Q$  make it possible to estimate, as well, the absolute value of the off-center displacement  $x_0$ ; the relationship between  $\nu_Q$  and  $x_0$ , necessary for this,

was obtained by van der Klink and Khanna (1984) by the use of the point-ion model and by taking into account polarization and repulsion forces. This yielded  $x_0 \approx 1.2 \text{ \AA}$ .

Thermal reorientations of Li should lead to averaging of the spectrum and disappearance of the quadrupole satellites at  $\nu > \nu_Q$ , which occurs at  $T > 50 \text{ K}$ . In this high-temperature region the modulation of the intercrystalline field gradient by the motion of the ion gives rise to nuclear spin-lattice relaxation. The reorientation frequency determined by spin-relaxation experiments (van der Klink *et al.*, 1983) agrees with the dielectric measurement data.

Since the reorientating impurities also affect the elastic properties of crystals, measurements of the velocity of sound in  $\text{KTaO}_3\text{:Li}$  have been undertaken (Höchli *et al.*, 1982; Smolensky *et al.*, 1983). The observed softening of the elastic moduli  $c_{11}$ - $c_{12}$  and lack of change in the modulus  $c_{44}$  argue for Li displacement along the [100] direction (with such a displacement, the off-center ion interacts only with the  $E_g$  deformation).

The reorientational dynamics of Li has also been investigated by the EPR method (Vugmeister *et al.*, 1984, 1987), axial  $\text{Fe}^{3+}$  centers having been used as paramagnetic probes. Because of the random spatial positions of Li relative to the paramagnetic probes, the EPR line was broadened by internal electric and elastic fields produced by the off-center ions. At low temperatures the broadening is quasistatic and nonuniform, and at  $T > 90 \text{ K}$ , where the  $\nu$  values are great enough, a dynamic narrowing of the line occurs, which is similar to the effect of averaging of the quadrupole structure in NMR. From the observed temperature dependence of the broadening, Vugmeister *et al.* (1984) determined the parameters  $\nu_0$  and  $U$ , which were in agreement with dielectric measurements.

The dielectric (Höchli and Baeriswyl, 1984) and EPR data permitted the effective dipole moment  $d^*$  of Li to be determined, which turned out to exceed by 20–30 times the intrinsic dipole moment  $d = ex_0$ . The EPR data show the  $d^*$  value to agree with the result  $d^* = \gamma \epsilon_0 d / 3$  presented in the preceding section [ $|\gamma| \approx 0.1$  in the point-dipole model (Vugmeister and Glinchuk, 1979)]. These findings, however, were strongly criticized by Höchli and Maglione (1989), who asserted, quoting Slater (1950), that  $\gamma$  is equal to zero for the Ba(K) site in the perovskites  $\text{BaTiO}_3$  ( $\text{KTaO}_3$ ). Apparently this assertion is based on a misunderstanding. Actually, the Lorentz factor  $\gamma$ , which did not figure at all in Slater's article (Slater, 1950), is the ratio of the local field acting at the given cubic site of the polarized lattice to the Lorentz form of the local field for a cubic crystal  $E_{\text{Lor}} = (4\pi/3)P$ , where  $P$  is the total polarization of the unit cell. Based on Slater's approach one can easily estimate Lorentz factors for different lattice sites. For example, for the Ba site we have according to Eq. (18) of Slater's article

$$\gamma_{\text{Ba}} = \frac{P_{\text{Ti}} + P_{\text{Ba}} + (1 - 3p)\bar{P}_{0a} + (2 + 3p)P_{0b}}{P_{\text{Ti}} + P_{\text{Ba}} + P_{0a} + 2P_{0b}},$$

where  $p = 8668/4\pi$ , and  $P_\alpha$  is the polarization for appropriate sublattices ( $P = \sum_\alpha P_\alpha$ ). Using the expressions for  $P_\alpha$  given on page 757 of Slater's article we obtain  $\gamma_{\text{Ba}} \approx -0.19$ . In the same manner it is easy to estimate the Lorentz factor  $\gamma_K$  for the K site of  $\text{KTaO}_3$ . For this purpose Vugmeister and Glinchuk (1979) used for oxygen and  $\text{K}^+$  polarizabilities the data of Tessman *et al.* (1953) leading to  $\gamma_K \approx -0.12$ . With the more exact values of K, Ta, and oxygen polarizabilities given by van der Klink and Khanna (1984), one can obtain  $\gamma_K \approx -0.13$ . A similar value,  $\gamma_K \approx -0.09$ , was obtained by Vihnin (1984), in contrast to an earlier mistaken assertion that  $\gamma_K = 0$  by Vihnin and Orlov (1983).

Specific features of the EPR linewidth's dependence on the Li concentration have also been observed (Vugmeister *et al.*, 1982, 1984) and shown to stem from an unusual dependence of the dipole-dipole interaction potential on the spacing between the off-center Li ions.

Thus the above experimental data convincingly show the off-center position of Li in  $\text{KTaO}_3$  and confirm the dipole-dipole interaction potential form [Eq. (3.11)], characteristic for highly polarizable crystals.

Note that it is quite clear that a decrease in repulsive forces and an increase in polarization forces for an impurity ion relative to the lattice ion it replaces favor the appearance of off-center positioning. Therefore, it is the impurities, whose ionic radius is smaller and polarization forces are greater, that generally become off-center ions. Experimental data on the polarizabilities of ions and parameters of repulsion made it possible to calculate the adiabatic potential for some impurities in alkali halide crystals (Dienes *et al.*, 1966; Wilson *et al.*, 1967; Quigley and Das, 1967, 1969, 1972) and in  $\text{KTaO}_3\text{:Li}$  (van der Klink and Khanna, 1984) and to show theoretically that off-centrality should indeed take place.

From the standpoint of electronic structure, off-centrality is encouraged by the existence of closely spaced levels of opposite parities. In this case the displacement of an impurity from a site (Glinchuk *et al.*, 1973) is promoted by the pseudo-Jahn-Teller effect (Bersuker, 1971), whose action is equivalent to that of polarization forces.

Höck and Thomas (1977); Höck, Schäfer, and Thomas, (1979) were the first to draw attention to the fact that in soft, highly polarizable lattices or in crystals with structural phase transitions, which exhibit a strong temperature dependence of lattice vibration frequencies, off-centrality (i.e., a multivalley pattern of the adiabatic potential) can occur below some well-defined temperature  $T_{\text{loc}}$ . This situation is sometimes called a "local phase transition" or "local freezing," as follows from a rough description based on the mean-field approximation. In actual fact, there is no freezing, but slow reorientations of the ions between different minima occur below  $T_{\text{loc}}$  (Höck *et al.*, 1979; Bruce and Cowley, 1981). The characteristic feature of the phenomenon is the temperature dependence of the activation barrier height in Eq. (4.1) [ $U = U(T)$ ].

When considering off-centrality as the result of the pseudo-Jahn-Teller effect it has been shown (Kristofel', 1979) that a temperature-dependent barrier between the off-center positions can also arise in ordinary weakly polarizable lattices.

We pass now to a discussion of cooperative effects in KTL.

Pure potassium tantalate is a virtual dielectric and exhibits paraelectric properties at any temperature. Its dielectric permittivity increases with lowering temperature, reaching  $\epsilon_0 = 5 \times 10^3$  at  $T = 4$  K. Introduction of Li ( $x > 1\%$ ) gives rise to a sharply defined permittivity peak, which shifts towards higher temperatures as the concentration of the off-center ions increases. We shall place primary emphasis here on the case of low Li concentrations, since it is in this field that a great body of contradictory data has been obtained and it has become the subject of controversy.

The first observation of dielectric anomalies in KTL appear to have been made by Davis, but these remained unpublished [the literature sometimes quotes a paper by Davis (1972) which, however, reports only the results for  $\text{KTaO}_3:\text{Na}$ ]. Yacoby and Just (1974) pointed out that dielectric anomalies resulting from the introduction of Li (and ascribed by these authors to the ferroelectric phase transition) could not be accounted for by a simple change in the size of the unit cell, caused by the impurity ions, as is often the case in virtual dielectrics. The addition of Li reduces the unit cell size (Yacoby and Just, 1974), but hydrostatic pressure experiments (Abel, 1971) have demonstrated that as the unit cell size decreases, so does the permittivity, and the crystal does not become ferroelectric. It is therefore natural to relate the anomalies in KTL properties to the off-center position of Li.

The earliest studies (Höchli *et al.*, 1979; Borsa *et al.*, 1980; van der Klink *et al.*, 1983) assumed the situation for  $\text{KTaO}_3:\text{Li}$  not to differ basically from that for  $\text{KCl}:\text{Li}$  right up to Li concentrations of  $x = 24\%$ . However, as will be seen below, even the dielectric experiments, whose results are the closest to the situation for alkali halide crystals, demonstrate that a substantial difference exists between these two classes of systems. Thus, in KTL, as in alkali halide crystals containing off-center ions, no spontaneous polarization has been detected by direct dielectric measurements, while residual polarization has

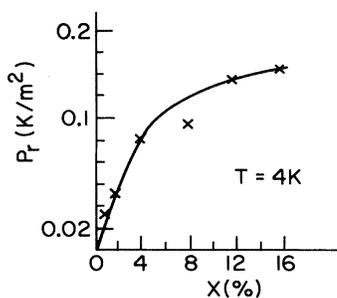


FIG. 14. Residual polarization in  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$  at  $T = 4$  K as a function of Li concentration. After Höchli *et al.*, 1978.

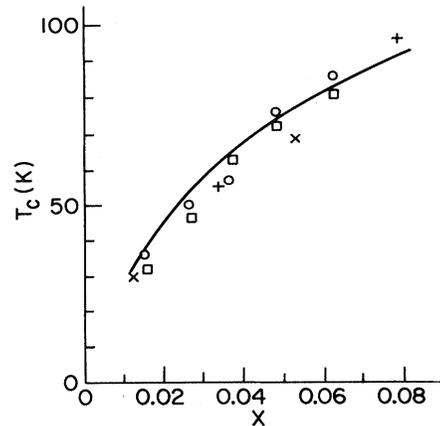


FIG. 15. Ferroelectric phase-transition temperature as a function of Li concentration in  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ , obtained by different methods:  $\circ$  birefringence;  $\square$ , dielectric measurements;  $+$  and  $\times$  Raman scattering. Solid curve corresponds to  $T_c = 300\sqrt{x}$  K. After van der Klink *et al.*, 1983.

been observed (Höchli *et al.*, 1978), whose increase slowed down with increasing  $x$  (Fig. 14). Such a dependence is substantially different from the relation  $P_r \propto x^2$  ( $x = na^3$ ) found for alkali halide crystals. The temperature dependence  $P_r(T)$  is also different: it rises rapidly (van der Klink *et al.*, 1983) at  $T < T_c$  ( $T_c$  is the temperature corresponding to the permittivity maximum, near which all Li concentration-dependent properties of the crystal are observed to exhibit anomalies). The concentration dependence of  $T_c$  is weaker than linear (Fig. 15), in contrast to the linear concentration dependence of Eq. (2.1).

At low Li concentrations, as the frequency decreases, the maximum of the frequency-dependent permittivity shifts towards lower temperatures (Fig. 16), but to a con-

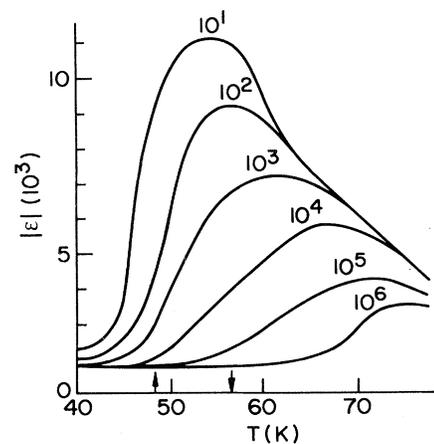


FIG. 16. Temperature dependence of frequency-dependent permittivity of  $\text{KTaO}_3:\text{Li}$ . Numerals at curves indicate frequencies in Hz;  $x = 0.026$ . After Höchli, 1982.

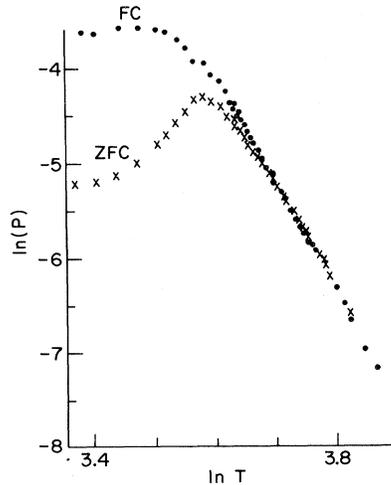


FIG. 17. Temperature dependencies of  $P_{FC}$  and  $P_{ZFC}$  for  $K_{0.984}Li_{0.016}TaO_3$  in external field  $E=30$  kV/m. After Torre, 1987.

siderably smaller extent than for  $KCl:OH^-$ . The frequency dispersion of the permittivity also exhibits other unusual properties.

Höchli *et al.* (1985) and Torre (1987) found that polarization irreversibility effects, characteristic of dipole glasses, show up at low temperatures. Thus there are differences between the field-cooled (FC) and the zero-field-cooled (ZFC) polarization (Fig. 17), which usually occurs in spin glasses, but, in contrast to  $KCl:OH^-$ -type dipole glasses, the FC polarization is time independent after the field is turned off (Fig. 18). Höchli *et al.* (1985) have also demonstrated that at  $x=0.016$  the “nonergodicity” temperature  $T_g$  (at which differences between the FC and the ZFC polarization begin) is dependent on the applied electric field  $E$ , as in spin glasses. These authors endeavored to interpret the dependence  $T_g(E)$  in terms of the equation derived by de Almeida and Thouless (1978),

$$E = [T_g(0) - T_g(E)]^\gamma,$$

for the model by Sherrington and Kirkpatrick (1975) with an infinite interaction range, which is not very relevant to the systems under consideration. Indeed, according to de Almeida and Thouless (1978),  $\gamma = 1.5$ .

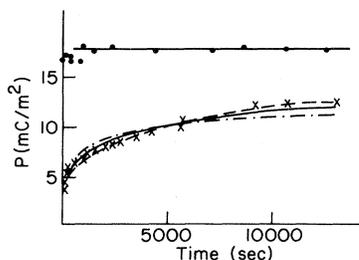


FIG. 18. Time dependence of residual polarization of  $K_{0.984}Li_{0.016}TaO_3$  ( $E=30$  kV/m;  $T=30.5$  K). After Höchli *et al.*, 1985.

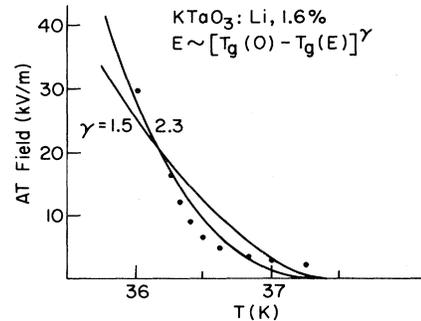


FIG. 19. Quasi-nonergodicity temperature  $T^*$  as a function of electric field for  $K_{0.984}Li_{0.016}TaO_3$ . After Torre, 1987.

Höchli *et al.* (1985) and Torre (1987) note that the agreement is better at  $\gamma=2.3$ . However, as is clear from Fig. 19, even in this case insufficient agreement with experimental results is observed to assert that a relation of the type  $E = [T_g(E) - T_g(0)]^\gamma$  holds. Experiments indicate only that  $T_g(E)$  decreases with increasing field.

Several studies (Poplavko *et al.* 1983; van der Klink *et al.*, 1983; Höchli and Baeriswyl, 1984; van der Klink and Borsa, 1984; Maglione *et al.*, 1987) have demonstrated that two different relaxation mechanisms responsible for dielectric dispersion show up at  $x > 0.04$ . A high-frequency relaxation mechanism has an activation energy  $U \approx 1000$  K and is associated with independent motions of the off-center ions (far from  $T_c$ ). A low-frequency mechanism whose nature is not yet clearly understood, is activated at an energy approximately 2.5 times higher. Characteristic frequencies of the two relaxation processes decrease as  $T \rightarrow T_c$  with a broadening of the relaxation time distribution. Smolensky *et al.* (1986) observed a splitting of the permittivity peak, ascribed by these authors to the motion of domain walls.

The above-presented experimental data, although demonstrating that the behavior of off-center ions in potassium tantalate differs from the situation in alkali halide crystals, proved inadequate to resolve the nature of the low-temperature state: ferroelectric or dipole glasses?—as in alkali halide crystals (at least, within a limited range of Li concentrations); so, at least, the question has been posed in the experimental studies under discussion. This point of view, stressing the similarities of the alkali halide systems, was expressed by Höchli *et al.* (1979), Geifman *et al.* (1981), Höchli (1982), and van der Klink *et al.* (1983), and, in the opinion of van der Klink *et al.* (1983), was also supported by experiments (Borsa *et al.*, 1980) where no anomalies in the rate of the spin-lattice relaxation near  $T_c$  were found.<sup>6</sup> Various groups of authors (Cornaz *et al.*, 1981; Courtens, 1981; Prater *et al.*, 1981a, 1981b; Yacoby, 1981; Chase *et al.*, 1982;

<sup>6</sup>There were no anomalies of the specific heat either (Lawless *et al.*, 1984; Strukov *et al.*, 1986).

Yacoby *et al.*, 1983; Vugmeister *et al.*, 1989) conducted additional experiments which greatly cleared up the nature of the phenomenon and enabled these authors to infer that ferroelectric domains with large regions of homogeneous spontaneous polarization are present in  $\text{KTaO}_3:\text{Li}$ .

For example, birefringence studies indicated that rather large polar regions appear below  $T_c$ , which have the form of domains of about 5000 Å in size (Prater *et al.*, 1981a, 1981b), oriented along the [100] direction and separated by irregularly arranged (Cornaz *et al.*, 1981) domain walls. It is clear that this picture is not consistent with traditional concepts of the dipole glass state, where the short-range order covers only a few nearest coordination spheres.

A still more convincing argument in favor of a ferroelectric phase transition in  $\text{KTaO}_3:\text{Li}$  at  $T = T_c$  was provided by the observation (Prater *et al.*, 1981a; Yacoby, 1981) of a splitting of the Raman scattering peak corresponding to the soft-mode frequency (peak B in Fig. 13), which clearly indicated a reduction in the symmetry of the low-temperature phase below  $T_c$ . The temperature dependence of the position of the Raman peaks for different Li concentrations is shown in Fig. 20, which also demonstrates that at  $T = T_c$  the soft-mode frequency has a finite value, this being characteristic for phase transitions of the order-disorder type.

An anomalous rise in the nonlinear dielectric response was found by Yacoby *et al.* (1983) to occur within a certain temperature range with increasing external electric field (Fig. 21); this is in contrast with  $\text{KCl}:\text{OH}^-$  dipole glass behavior, for which the anomalies are smoothed out in the electric field. At the same time, it was shown by these authors that the character of the dielectric anomalies was in complete agreement with the assumption that a ferroelectric phase transition of the first type took place, whereas above  $T_c$  the dielectric nonlinearity

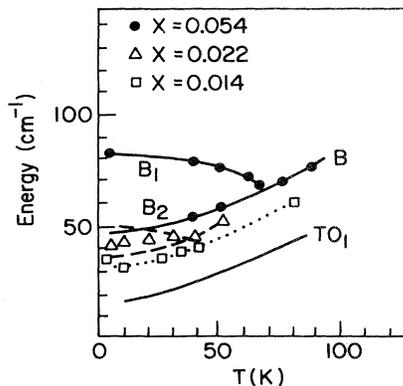


FIG. 20. Temperature dependence of soft-mode energy of  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$  and of pure  $\text{KTaO}_3$  (curve  $\text{TO}_1$ ). Vertical bars indicate the magnitude of unresolved splitting at  $x = 0.022$ . After Prater *et al.*, 1981b.

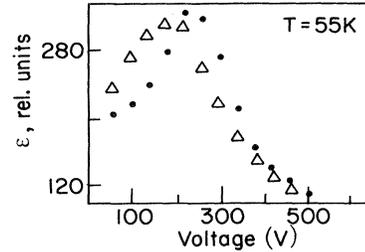


FIG. 21. Permittivity of  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$  at  $x = 0.035$  as a function of applied voltage: ●, increasing voltage; △, decreasing voltage. After Yacoby *et al.*, 1983.

factor<sup>7</sup>  $b_1$  changed its sign. Indications of a first-order transition were also found in earlier experiments (Courten, 1981). Vugmeister (1984b) has shown the appearance of the first type of phase transition to be associated with additional electrostrictional interactions in a crystal containing impurities, which stem from the fact that the off-center Li ion has not only an electric, but also an elastic quadrupolar moment.

The acoustic anomalies discovered by Chase *et al.* (1982) and Smolensky *et al.* (1983) argue as well in favor of a ferroelectric ordering.

The observation of a shift of the EPR line of the cubic center of  $\text{Fe}^{3+}$  at  $x = 0.045$ , proportional to the square of the spontaneous polarization (Vugmeister *et al.*, 1989), is additional evidence of a reduction in the low-temperature phase symmetry.

Andrews (1985) investigated structural changes in KTL by the use of the x-ray scattering technique, which allows structural changes in a crystal and the amount of spontaneous deformation to be directly observed from the splitting of the Bragg peaks. The temperature dependence of the lattice parameter, measured in this way, is shown in Fig. 22, where it can be seen that the splitting of the Bragg peak at  $x = 0.05$  is clearly defined; this enabled Andrews to determine the tetragonal deformation of the lattice. The obtained  $c/a$  ratio amounted to  $1.00138 \pm 0.0005$  at 10 K. Andrews noted that the absence of Bragg-peak splitting at  $x = 0.016$  was due to the small magnitude of the spontaneous deformation, which at  $x = 0.016$  should be 25 times smaller than at  $x = 0.05$ . At the same time, experiments on diffuse scattering of x rays, conducted by this author, indicate that homogeneous deformation regions with an average size of at least 1000 Å exist in the crystal even at  $x = 0.016$ . This conclusion was supported by subsequent experiments (Kamitakahara *et al.*, 1987) using neutron diffraction, where specimens with concentrations of  $x = 0.017$  and  $x = 0.04$  were investigated; the intensity of the Bragg reflections was measured as a function of temperature. The two

<sup>7</sup>The factor in the term  $(\frac{1}{4})b_1P^4$  of the crystal free energy.

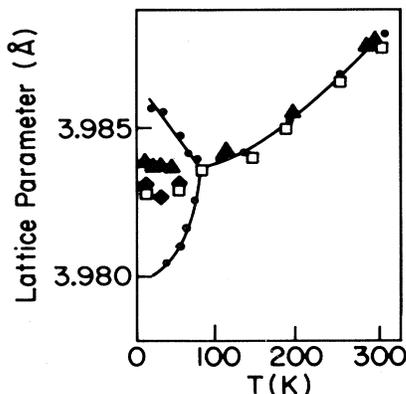


FIG. 22. Temperature dependence of lattice parameter in KTL. After Andrews, 1985.

specimens exhibited qualitatively identical effects due to the presence of a cancellation relief. These authors asserted that this effect would not be noticeable if the two crystals had not contained homogeneous polarization regions of at least 1000 Å. However, in contrast to ordinary ferroelectrics, the specimen with  $x = 0.017$  also exhibited long-time relaxation phenomena characteristic of dipole glasses; namely, after cooling to below 40 K, the intensity of the Bragg reflexes reached their final values within several hours. The temperature dependence of the Bragg peaks is presented in Fig. 23.

Summarizing this brief review of the experimental situation for  $\text{KTaO}_3\text{:Li}$ , which is typical of highly polarizable crystals containing dipole impurities, we may say that the basic features of the experimentally observed phenomena, the coexistence of ferroelectric domains and long-time relaxation effects, are in qualitative agreement with the theoretical concepts presented in the preceding section. The principal distinction of these systems is the existence of a disordered configuration of impurities, which results in phenomena more complex than those predicted by the self-consistent field approximation. A specific role is played by clusters of dipoles separated by less than aver-

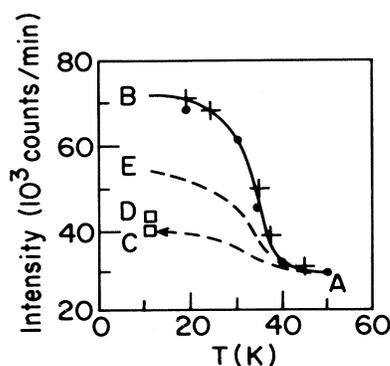


FIG. 23. Temperature dependence of Bragg intensities in KTL. After Kamitakahara *et al.*, 1987.

age spacings, whose relaxation is impeded as described in Sec. II B. It was noted (Vugmeister, 1984a) that such closely spaced dipoles may be treated as quasistatic defects<sup>8</sup> which, according to the theory of Imry and Ma (1975), should lead to division of the crystals into domains, the latter originating not only in spherical-symmetry systems (Imry and Ma, 1975), but also in anisotropic ones (Imry and Wortis, 1979). Dipole glass and domain states are similar in that polarization by an external field after cooling in a zero field is difficult to produce in both cases. Residual polarization after cooling in a constant field and long-time relaxation exist in both these cases.

It should, however, be pointed out that the long-time relaxation effects in  $\text{KTaO}_3\text{:Li}$  are far more pronounced than could be expected from the cluster model of the formation of frozen defects. Indeed, the probability that strongly coupled clusters of particles will form at less-than-average distances is high at concentrations  $x$  not greatly exceeding the critical concentration  $x_{cr} \sim 10^{-3}$  [Eq. (3.33)], while with Li in  $\text{KTaO}_3$  cooperative effects, can be observed only at  $x > 0.01$ , due to an extremely slow single-particle relaxation of Li at  $T < 30$  K [in accordance with Eq. (4.1)].

Some new ideas concerning this problem have been suggested by Kleemann *et al.* (1987), who reported new data on birefringence and dielectric permittivity at Li concentrations of  $x = 0.011$ , 0.016, and 0.063. These authors note that, since single-particle relaxation of Li even at  $T \approx 40$  K is very slow, hence, by virtue of the distribution of relaxation times, a large proportion of single dipoles that may be regarded as frozen with respect to the remaining dipoles may well exist. The relative number of frozen dipoles would be greater the lower the temperature. They stated that the boundary concentration  $x_{cr}$  between a true dipole glass of the  $\text{KCl:Li}$  type and the domain states could be determined from the birefringence data and made the estimate  $x_{cr} \approx 0.02$ . Such a critical concentration value substantially exceeds the theoretical estimate (3.33) and agrees with the suggestion that additional static random fields (not to be confused with dynamical random fields caused by reorienting Li dipoles) play an important role in the ordering phenomena in  $\text{KTaO}_3\text{:Li}$ . At the present time we can consider it as established that the existence of static random fields leads to destruction of the long-range order in three-dimensional Ising-like systems ( $\text{KTaO}_3\text{:Li}$  is such a system) only when the width of the static random-field probability distribution exceeds its definite critical value. The conditions for destruction of long-range order by

<sup>8</sup>The second low-frequency dispersion of the dielectric response in KTL, which appears to be associated with closely spaced dipole clusters, supports this assumption (Höchli and Baeriswyl, 1984).

static random fields for the Ising model were first analyzed by Schneider and Pytte (1977) for spin systems based on the mean-field approximation of the spin-spin interaction (dipole-dipole interaction in our case). It is clear, however, that in the system under consideration when ordering dipoles are randomly located in the lattice sites, the random-field theory developed here is more appropriate.

As one can show (Vugmeister and Stefanovich, 1990), in order to take into account the static random field we should replace  $F_1(\rho)$  in Eq. (3.37) with

$$\tilde{F}_1(\rho) = F_1(\rho) + F_1^{\text{RF}}(\rho),$$

where  $F_1^{\text{RF}}(\rho)$  is the logarithm of the Fourier transformation of the static random-field probability distribution. Estimates based on Eq. (3.37) (Vugmeister and Stefanovich, 1990) show that in order to get an experimental critical concentration  $x_{\text{cr}} \approx 0.02$ , the width of the random-field probability distribution should be put approximately equal to the width of the  $f(E)$  function (3.25). This value is much greater than one can assume if frozen Li dipoles are the only source of static random fields. Therefore we can conclude that additional defects of unknown chemical composition, perhaps the same as have been observed in Raman scattering experiments (Uwe *et al.*, 1986), are responsible for the ferroelectric critical concentration in  $\text{KTaO}_3:\text{Li}$ .

Moreover, the dilatational part of the strain field induced by off-center ions can be the source of static random fields. The concept of static random fields is able to provide a natural explanation of the domain states in  $\text{KTaO}_3:\text{Li}$  because nowadays it is well known that, in spite of the prediction of thermodynamic theory (Imry and Ma, 1975; Imbrie, 1984) that long-range order in the three-dimensional case does exist for a vanishingly small static random-field probability distribution, such an equilibrium state is not reached in random-field cooled experiments. Instead we have metastable domain states in which domain walls are pinned by the random fields. The long-time relaxation observed in  $\text{KTaO}_3:\text{Li}$  and developing in experiments much more distinctly than predicted by the simple theory of Sec. III may also be caused by metastable domain states. Recently Schremmer *et al.* (1989) have shown that domain states in  $\text{KTaO}_3:\text{Li}$  can be oriented by an external electric field leading to the appearance of an additional maximum in dielectric permittivity (after switching off the field), which Schremmer *et al.* (1989) considered as evidence of a true ferroelectric phase transition. The smeared permittivity peak observed earlier at  $E_{\text{ext}} = 0$  is of the relaxational type, in the opinion of these authors. It should be mentioned, however, that such an interpretation is in contradiction with the point of view of Yacoby *et al.* (1983), and therefore additional investigations are needed to clear up the question. Note also that the existence of domain states induced by static random fields can smear a ferroelectric phase transition, as was observed, for example, in the mixed system  $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$  with off-center Ca ions

(Bednorz and Müller, 1984; Kleemann, Kutz, *et al.*, 1988; Kleemann, Schremmer, and Rytz, 1989). Ca doping leads to the appearance of two kinds of defects in  $\text{SrTiO}_3$ : reorienting and frozen dipoles (Kleemann, Kutz, *et al.*, 1988). Reorienting dipoles (off-center ions) are created initially when one increases the Ca concentration, which leads to an increase in the ferroelectric transition temperature. However, a further increase in Ca concentration leads to formation of frozen dipoles and smearing of the ferroelectric transition. Random-field-induced domain states in  $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$  are orienting in an external electric field even at  $T = 0$  (Kleemann, Kutz, *et al.*, 1988).

In recent years the role of elastic interactions between off-center ions in  $\text{KTaO}_3$  and the effects of quadrupolar ordering have been discussed extensively. Although these questions are beyond the scope of this review, which is primarily concerned with the ordering in polarizable media associated with the electric dipole-dipole interaction, we shall mention them briefly because they are now of interest.

How strong is the interaction between elastic quadrupoles and is a ferroelastic phase transition possible here? These questions are important because if a ferroelastic phase transition is more readily attainable than a ferroelectric one, the theory presented above should be corrected to describe more accurately the ordering phenomena in real crystals.

Ultrasound absorption experiments (Höchli *et al.*, 1982) made possible an estimate of the coupling parameter  $g$  between the elastic quadrupole moment of a Li ion and the strain field in  $\text{KTaO}_3$ . The temperature  $T_Q$  of quadrupole ordering in the mean-field approximation is equal to

$$k_B T_Q = g^2 n / 3c,$$

where  $C = C_{11} - C_{12}$  is the elastic modulus of the host lattice. Taking into account that, according to Höchli *et al.* (1982),  $g \approx 1.7 \times 10^{-12}$  CGSE we have  $T_Q < 5$  K for Li concentrations less than 10 at. %, which is much less than typical values of the ferroelectric transition temperature at these concentrations.

Glinchuk and Smolyaninov (1988, 1989) took into account that the interaction of quadrupole moments with lattice polarization of the type  $V_Q = \sum_{\alpha\beta} Q_{\alpha\beta} P_\alpha P_\beta$  leads to additional indirect quadrupole-quadrupole interactions, which can be significant in a soft lattice. Moreover, the isotropic term in such an indirect interaction appears similar to the isotropic term in dipole-dipole Hamiltonian (3.11) for a ferroelastic phase transition. But the numerical estimate of Glinchuk and Smolyaninov (1988, 1989) showed that indirect quadrupole-quadrupole interaction does not increase  $T_Q$  significantly in  $\text{KTaO}_3:\text{Li}$  and therefore a ferroelastic phase transition does not occur here, at least for  $x \lesssim 0.1$ . Glinchuk and Smolyaninov (1990) have investigated some additional peculiarities connected with an internal elastic field in mixed crystals.

An essential feature of the system under consideration is that host-lattice tetragonal distortions in the low-temperature phase are not completely homogeneous, but the distribution of the strain field created by off-center ions may be observed in neutron (Höchli, Doussineau, and Ziolkievich, 1989) and EPR (Pechenyi *et al.*, 1989 experiments, Kleemann, Schafer, *et al.*, 1988); see also Kleemann *et al.*, 1987) observed a logarithmic time dependence of the birefringence, ascribed by them to the manifestation of quadrupolar ordering. The remarkable feature of these results is that such quadrupolar ordering exists even below the critical concentration  $x_{cr} \approx 0.02$ . As was pointed out by Kleemann, Schafer, *et al.* (1988), the observed phenomena can be attributed to local tetragonal distortion induced by internal strains. However, as they rightly noted, substantiation of this hypothesis calls for experiments on the effects of pressure.

The present authors are inclined to the opinion, based on the strength of the available experimental evidence and on the estimate of Eq. (3.33), that domain states whose sizes fluctuate greatly at low Li concentrations, where the mean-field theory is invalid, occur in  $\text{KTaO}_3:\text{Li}$  over the entire range of  $x \geq 0.02$ .

An obvious success of the theory is its good description of the observed concentration dependence of the phase-transition temperature using a single theoretical parameter, the quantity  $\gamma d$ , where  $d$  is the dipole moment of Li and  $\gamma$  is the parameter of the local field at the location of the Li (see Sec. III). Comparing the theory with experimental results (Vugmeister, 1985; Vugmeister and Stefanovich, 1987a), yielded  $|\gamma|d \approx 0.08 e \text{ \AA}$ , which excellently agrees with the EPR data (Vugmeister *et al.*, 1984) of  $\gamma d = 0.1 e \text{ \AA}$ . Taking into account the NMR data (van der Klink and Borsa, 1984) on the off-center displacement  $X_{0\text{Li}} \approx 1 \text{ \AA}$ , this allows us to state that the local-field parameter value  $|\gamma| \approx 0.1$  at the Li location is well enough (even unexpectedly) predicted by a purely ionic model within the framework of the Slater (1950) theory for a perovskite lattice.

## B. $\text{KTaO}_3:\text{Nb}$ (KTN)

It is at present clear that the behavior of potassium tantalate with Nb differs little in principle from the situation with Li. At Nb concentrations  $x \gtrsim 0.02$  the experiments give evidence for the existence of ferroelectric domains, whereas symptoms of dipole glass, showing up as long-time relaxation, appear at  $0.008 < x < 0.02$ . Historically, the experimental study of phenomena in  $\text{K}_{1-x}\text{Nb}_x\text{TaO}_3$  (KTN) proceeded in the opposite order to that of KTL. The first dielectric and acoustic measurements (Triebwasser, 1959; Kind and Müller, 1976; Boatner *et al.*, 1977; Höchli and Boatner, 1979; Rytz *et al.*, 1980, 1983) assumed that a ferroelectric phase transition, which had been shown to begin at the critical concentration  $x_{cr} = 0.008$ , took place in KTN. At close-

to-critical concentrations the behavior of the critical temperature  $T_c$ , permittivity, and other physical quantities differed considerably from the predictions of mean-field theory; this was attributed to the manifestation of quantum fluctuation effects (see also Müller, 1985). As an example, Fig. 24 shows the dependence of the maximum permittivity temperature (assumed equal to  $T_c$ ) on the Nb concentration. It can be seen that at  $x > 0.05$  the dependence  $T_c(x)$  is practically linear, whereas at low concentrations it is  $T_c(x) \propto (x - x_{cr})^{1/2}$ , which is typical for quantum ferroelectrics (Oppermann and Thomas, 1975; Schneider *et al.*, 1976).

In the earlier studies mentioned above an attempt to describe the phase transition in KTN in the framework of the quantum ferroelectric model was undertaken and it was suggested that the niobium impurity was situated in the usual slightly anharmonic potential. But such a treatment did not describe the observed concentration dependence of the phase-transition temperature  $T_c(x)$  without the additional assumption of strong temperature dependence of the local niobium frequency (Kugel *et al.*, 1987). The possibility of such a strong temperature dependence follows from a model of Migoni (Migoni *et al.*, 1976) in which the nonlinear polarizability of oxygen ions is taken into account explicitly. But such an approach does not account for the appearance of relaxational dynamics in KTN at low temperatures, which we shall discuss below. Vugmeister and Antimirova (1990) suggested that the crossover from an order-disorder-type phase transition to a displacive one takes place with increasing Nb concentration. To describe such a phase transition a semiphenomenological approach was used with the assumption that the Nb is moving in an eight-well off-center potential with sufficiently low barrier. The barrier height  $U \approx 60 \text{ K}$  and off-center displacement  $X_0 \approx 0.08 \text{ \AA}$  of the Nb ions were estimated by the best fit to  $T_c(x)$  experimental data (Fig. 24).

It should be mentioned that because of the large covalency of the Ta—O, Nb—O bonds, the Slater theory

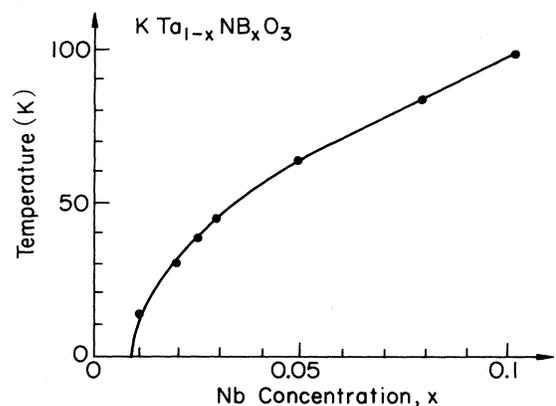


FIG. 24. Temperature of permittivity maximum as a function of Nb concentration. After Müller, 1985.

(Slater, 1950) is not applicable to KTN, in contrast to KTL (Vugmeister and Antimirova, 1990).

A series of optical experiments similar to the KTL studies were conducted in an effort to gain a deeper understanding of the nature of the phase transition and of the mechanism by which a low Nb impurity concentration changes the properties of the crystal so drastically. The first study of KTN using Raman scattering was carried out by Manlief and Fan (1972). Yacoby (1978) observed at  $x=0.06$  Raman scattering of the first order, resulting from "rigid"  $\text{TO}_2$  phonons. The possibility of such first-order scattering, forbidden for a pure crystal by the selection rules, was ascribed to the fact that Nb produces in an odd-symmetry crystal microdeformations that cover a few lattice constants. This opinion was supported by detailed experiments and calculations conducted by Uwe *et al.* (1986), who observed peaks of the first-order scattering from low-frequency soft phonons of the  $\text{TO}_1$  branch for various wave-vector values. They investigated  $\text{KTaO}_3$  both pure and doped with SR and Ca impurities. These authors demonstrated that regions polarized by defects, regions whose size  $r_c \approx 4a$  at low temperatures and  $r_c \approx 1.3a$  at  $T=100$  K (where  $a$  is the lattice constant), do indeed exist in the crystal. Such a point of view is fully identical, both qualitatively and quantitatively, to the theoretical concepts discussed in Sec. III A [see, for example, Eq. (3.18)], where the size of defect-polarized regions was related to the correlation radius  $r_c$  for a pure crystal. Using the definition  $r_c = s/\omega_0$  [Eq. (3.8)], presented in Sec. III A, and taking the values of the soft-mode frequency  $\omega_0$  and  $s$  from the study by Axe *et al.* (1970), we obtain for  $r_c$  about the same numerical estimates as those reported by Uwe *et al.* (1986).

The definition of the polarized regions in KTN by Nb alone rather than by other impurities was contested by Prater *et al.* (1981a, 1981b) who observed no dependence of the first-order scattering intensity on the Nb concentration. These authors claimed that the presence of Nb results only in softening the soft-mode frequency, i.e., in inducing a ferroelectric phase transition, whereas the appearance of the first-order scattering peak was ascribed by them to the interaction of the optical  $\text{TO}_1$  mode with the acoustic TA branch; they attributed the effect of Nb on the intensity of the  $\text{TO}_2$  mode close to  $T_c$  to the smearing of the phase-transition temperature in different ferroelectric domains. The opinion of Yacoby (1978) may, however, happen to be valid if  $\omega_{\text{TO}_1} < \nu < \omega_{\text{TO}_2}$  (where  $\nu$  is the frequency of the fluctuational motion of Nb) close to  $T_c$ . In this case, Nb will induce the first-order scattering spectrum associated with the  $\text{TO}_2$  mode alone. This opinion is borne out by subsequent, more precise, experiments (Lee *et al.*, 1985; Lyons *et al.*, 1986), which indeed demonstrated that, in accord with Prater *et al.* (1981), the intensity of the first-order scattering by the  $\text{TO}_1$  mode is independent of the Nb concentration at temperatures above 20 K, but exhibits a strong concentration dependence below 20 K. In the opinion of Lyons *et al.* (1986), this is due to a strong tem-

perature dependence of the Nb fluctuation frequency below 20 K.

Prater *et al.* (1981a, 1981b) employed two different techniques to determine the phase-transition temperature. One of these was to observe the change in the Raman spectrum at  $T < T_c$ . Such a change is illustrated in Fig. 25, which shows an intense peak in the first-order scattering by the  $\text{TO}_1$  mode appearing below  $T_c$ . With decreasing temperature the intensity of the peak increases and it shifts towards higher energies. Splitting of the peak into two peaks was observed at  $T=4.2$  K in specimens containing 3% Nb and more. As  $T_c$  is approached, the frequency of the soft  $\text{TO}_1$  mode decreases, as it should for a displacement-type transition [this has also been detected in neutron experiments (Fontana *et al.*, 1984)]. However, at  $T \rightarrow T_c$  the soft-mode frequency does not go below  $10 \text{ cm}^{-1}$ , this was taken as evidence of a central peak, which has been studied in greater detail by Lee *et al.* (1985) and Lyons *et al.* (1986).

Prater *et al.* (1981) also observed the depolarization of light. In the cubic phase the optical properties of the crystal are isotropic, and there is no depolarization. It arises in the presence of optically anisotropic ferroelectric domains because of repeated changes in the polarization from different domains (Fig. 26). Depolarization experiments clearly demonstrate the existence in KTN of ferroelectric domains whose sizes exceed the wavelength

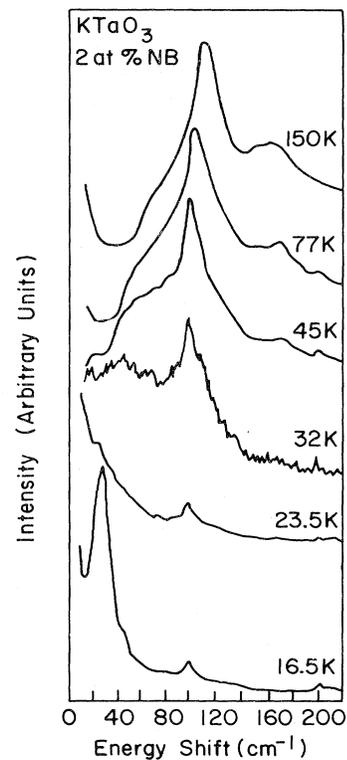


FIG. 25. Raman spectrum transformation with decreasing temperature for  $\text{KTa}_{0.98}\text{Nb}_{0.02}\text{O}_3$ . After Prater *et al.*, 1981a.

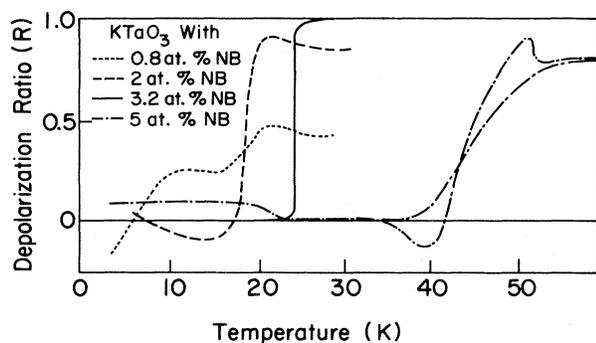


FIG. 26. Temperature dependence of the degree of depolarization of light after passage through KTN containing different Nb concentrations. After Prater *et al.*, 1981a.

of light and which differ somewhat in their phase-transition temperatures. At  $x \lesssim 0.02$ , however, the polarization is incomplete even at  $T=4.2$  K, which indicates that either the anisotropy in every domain is small or only a small part of the specimen has transformed into ferroelectric domains.

A decrease in symmetry below  $T_c$  is also indicated by hyper-Raman experiments on second-harmonic generation (Kugel *et al.*, 1984). A firm conviction existed till 1984 that a displacement-type ferroelectric phase transition to a rhombohedral symmetry phase at  $x \lesssim 5\%$  (Boatner *et al.*, 1977) occurred in KTN, with indications of a defect-induced central peak corresponding to the theory of Halperin and Varma (1976). The dependence of the soft-mode frequency on the Nb concentration and on the temperature was explained in terms of a shell model in which the strong electronic polarizability of an oxygen ion played a substantial part (see Kugel *et al.*, 1985, 1987, 1988, where references to earlier studies are presented).

Samara (1984, 1985) was the first to strike a major blow at the established concepts on the character of the phase transition in KTN. At a Nb concentration  $x=0.009$  he observed a low-frequency (right to  $10^2$  Hz) dispersion of permittivity at  $T < 10$  K (Fig. 27), which could be accounted for if thermal fluctuations of Nb at low temperatures were of an activation character. This meant that Nb at low temperatures is an off-center ion, i.e., a reorienting dipole defect. Analysis of the dispersion curves permitted the magnitude of the activation barrier  $U$  in Eq. (4.1) to be determined, which turned out to be  $U \approx 60-70$  K (Samara, 1985; Glinchuk *et al.*, 1987). This conclusion by itself only defined more exactly the character of the individual motion of Nb at low temperatures and did not contradict the possibility of a ferroelectric phase transition; an order-disorder phase transition can be accomplished at low temperature because of slow Nb motion. A difficulty arose, however, in interpreting the experimental data, reported by Samara, in terms of the ferroelectric phase transition; it arose when one attempted to match within the framework of Eq. (4.1) such a low Nb reorientation frequency at low

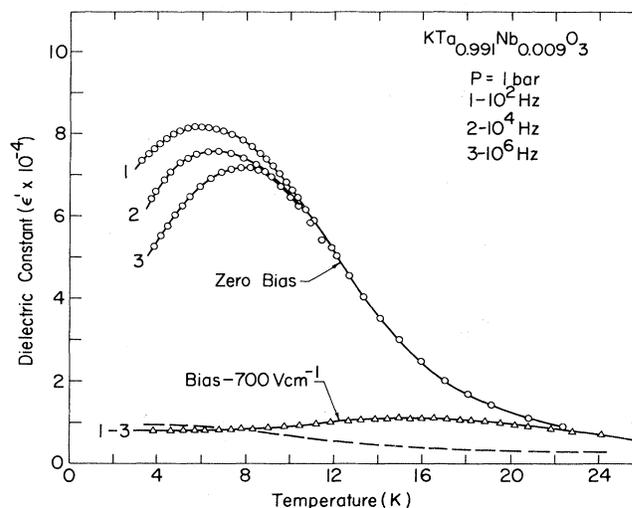


FIG. 27. Temperature dependence of the real part of the dielectric constant of KTN ( $x=0.009$ ) crystal, showing a strong frequency dispersion. After Samara, 1985.

temperatures, observed by Samara, with the results of Raman experiments at high temperatures, which show the Nb motion frequency to be not less than  $10^{10}-10^{12}$   $s^{-1}$ . Processing the dielectric and the Raman experiments, based on Eq. (4.1), yielded  $\nu_0 \sim 10^{21}$   $s^{-1}$ , which has no physical meaning. Due to this, Samara (1984, 1985) suggested that a cooperative freezing mechanism affecting the Nb motion goes into action at low temperatures, which is similar to the situation for spin glasses (Binder and Young, 1986). Further study of the mechanism of such a cooperative freezing was undertaken by Lyons *et al.* (1986, 1987). In the 1986 paper, as has been noted, Lyons *et al.* investigated in detail the dependence of the first-order Raman scattering intensity on the Nb concentration at  $x=0.009$ . They observed a pronounced central peak, which showed up not only at  $T \approx T_m$  ( $T_m=6-7$  K is the temperature corresponding to the permittivity maximum), but also right up to  $T=14$  K (Fig. 28). This indicated that the central peak stemmed from reorientational motion of Nb. The temperature dependence of the central peak width, which, in the opinion of Lyons *et al.* (1986), determines the averaged frequency of reorientations of Nb-induced clusters, was approximated by the Vogel-Fulcher law

$$\nu = \nu_0 \exp[-U/(T - T_0)], \quad (4.2)$$

with physically reasonable parameters  $U=70$  K,  $T_0=3$  K, and  $\nu_0=300$   $cm^{-1}$  (see also Glinchuk *et al.*, 1987). However, in deriving Eq. (4.2), Lyons *et al.* (1986) neglected the possibility that an interaction between impurities might affect the distribution of reorientation frequencies. Such a spread of reorientations, resulting in a logarithmic time dependence of various physical quantities, is, as has been shown in Secs. II B and IV A, rather substantial both in classical dipole glasses, such as

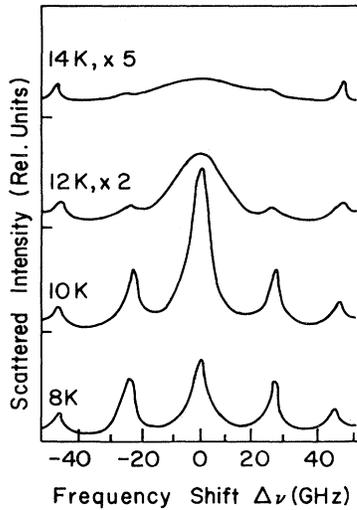


FIG. 28. Spectrum with a central peak in a zero field at different temperatures. After Lyons *et al.*, 1986.

KCl:Li,  $\text{OH}^-$ , and in the case of  $\text{KTaO}_3\text{:Li}$ . Recent experiments (Lyons *et al.*, 1987) have demonstrated that  $\text{KTaO}_3\text{:Nb}$  is not an exception in this respect. The latter authors undertook a study to determine the extent of the analogy between cooperative phenomena in KTN and in spin glasses. Their principal goal consisted in ascertaining the behavior of the nonlinear dielectric susceptibility, which they believed to be a test for dipole glass behavior. Although, as can be seen in Fig. 29, the nonlinear susceptibility exhibits a clearly defined maximum, in the case under consideration this is not an unambiguous indication of an equilibrium phase transition to the dipole glass state, since a similar behavior should also be observed in the presence of ferroelectric domains [the possibility of whose existence at  $x=0.009$  is not denied (Kleemann *et al.*, 1985)], as follows from an analysis in terms of the mean-field theory.

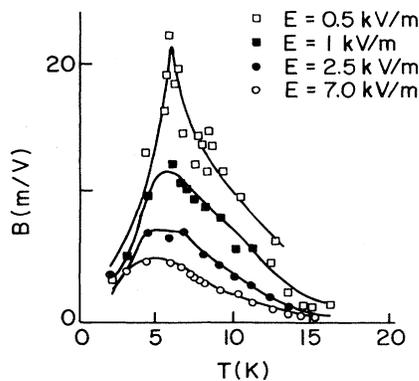


FIG. 29. Value of coefficient  $B$  in Eq. (4.3) for  $E\parallel[111]$  (Lyons *et al.*, 1987).

Lyons *et al.* (1987) discovered that at arbitrarily low values of the applied electric field  $E$  the polarization  $P(E)$  induced by the field is a nonlinear function of  $E$  and is described by the relation

$$P(E) = \chi_{1,ZFC}E + \text{sign}(E)BE^2, \quad (4.3)$$

where the coefficient  $B$  is given in Fig. 29. After the field is turned off, the polarization decays according to the logarithmic dependence

$$P(t) = P_0 + P_1 \ln(t\nu_0)$$

over the entire temperature range from 1.8 to 15 K. This behavior is obviously inconsistent with a description in terms of the Vogel-Fulcher law and indicates a cluster mechanism associated with slow relaxation of closely spaced Nb dipoles, similar to the situation for KTL. Lyons *et al.* noted that the cluster model provides an explanation not only of the logarithmic relaxation, but also of Eq. (4.3). It should be mentioned, however, that the experimental procedure used by Lyons *et al.* (1987) differs from the method used in spin glasses and electric dipole glasses. Usually one increases the static field while measuring the ac complex susceptibility at optimal frequencies. Different experimental techniques can lead to different results.

Sommer and Kleemann (1990) have performed careful measurements of frequency-dependent dielectric permittivity for different temperatures. They established that the frequency dependence of the permittivity can be described by the superposition of two independent relaxation mechanisms: (i) a monodispersive relaxation process, which the authors ascribed to reorientation of individual Nb ions surrounded by clouds of host-lattice polarization; (ii) a polydispersive relaxation process, which Sommer and Kleemann (1990) connected with the glassy state due to the interaction between different Nb ions. No signs of the Vogel-Fulcher law were observed.

A similarly complicated picture of Nb relaxation consisting of two different relaxation mechanisms was observed by electron paramagnetic resonance (Pechenyi *et al.*, 1988; Antimirova *et al.*, 1990). The continuous saturation EPR experiment described by Pechenyi *et al.* and Antimirova *et al.* revealed an additional low-frequency ( $\sim 10^8$  Hz) dynamics. It was shown that this phenomenon is connected with reorientation of the elastic degree of freedom of the off-center ions.

Sommer and Kleemann (1990) have also been observing stretched exponential temporal decay of the permittivity after quenching the sample and exposing it to an external electric field or to the built-in long-range stress fields accompanying lattice strains (due to crystal growth, cutting, and polishing).

Kleemann *et al.* (1985), have demonstrated, on the basis of the birefringence data and measurements of the refractive index, that ferroelectric domains exist in KTN at  $x=0.012$ , the polarization fluctuations in the domains being, however,  $\langle P^2 \rangle > P_s^2$  (where  $P_s$  is the spontaneous polarization). The  $\langle P^2 \rangle / P_s^2$  ratio found by them corre-

lates with the EPR data (Vugmeister *et al.*, 1988).

There are no specific-heat anomalies in KTN, as in KTL (Lawless *et al.*, 1981, 1985); however, in contrast to KTL, a critical increase in the spin-lattice rate of the K nuclei, indicating a phase transition, was observed in KTN at  $x=0.02$  by van der Klink *et al.* (1986). Using data on the concentration dependencies of intensities of the NMR signal of the Nb and Ta nuclei, these authors were able to demonstrate that in the low-temperature phase all the Nb ions displace from the lattice sites, which is not the case for Ta: only those Ta ions displace that are close to Nb, at a distance on the order of the correlation radius  $r_c$ , so that every Nb ion polarized an adjacent region containing 100 unit cells of the crystal. But in the paper by Rod *et al.* (1988) a displacement of the order of  $0.04 \text{ \AA}$  was reported for all Ta ions. Moreover, according to Rod *et al.* (1988), this phenomenon takes place in  $\text{KTaO}_3$  containing defects as well as in pure  $\text{KTaO}_3$ . The displacement of Nb ions  $x_0 \approx 0.15 \text{ \AA}$  obtained by these authors is in agreement with the estimate of Vugmeister and Antimirova (1990)  $x_0 \approx 0.08 \text{ \AA}$ .

### C. $\text{KTaO}_3:\text{Na}$

Our understanding of cooperative phenomena occurring when Na atoms are substituted for K in  $\text{KTaO}_3$  evolved in approximately the same way as for KTN, but far fewer experimental studies have been conducted with  $\text{KTaO}_3:\text{Na}$  than with KTN and KTL, and therefore the character of the phenomena occurring here is at present much less clear.

The first studies of mixed  $\text{K}_{1-x}\text{Na}_x\text{TaO}_3$  crystals were conducted by David (1972) and Perry and Tornberg (1969). Investigating the dielectric and the soft-mode properties, they demonstrated that the ferroelectric phase-transition temperature  $T_c$  first rises to the value  $T_c = 65 \text{ K}$  at  $x = 0.48$  and then decreases. A large number of studies have been conducted in the range  $0 < x < 0.28$ , where departures from classical ferroelectric behavior, similar to the situation for KTN, were observed. The departures have been interpreted as manifestations of quantum fluctuations, known to be substantial at low temperatures. In the quantum region it has been found that  $T_c \propto (x - x_c)^{1/2}$ , where the critical concentration of the ferroelectric phase transition is  $x_c = 0.012$ .

The off-center position of Na in  $\text{KTaO}_3$  was first determined in a pioneering study by Yacoby and Just (1974). Nuclear-magnetic-resonance studies (Höchli and Rigamonti, 1983; van der Klink and Rytz, 1983; Rigamonti and Torre, 1986) made it possible to determine from the spin-lattice relaxation the amount of the off-center displacement  $x_0$ , which turned out to be very small:  $x_0 \approx 0.04 \text{ \AA}$ . The off-center position of Na completely disappears at  $T_{\text{loc}} = 200 \text{ K}$ . The NMR studies also determined the most probable frequency of Na reorientations, which satisfies Eq. (4.1) with the parameters  $\nu_0 = 2 \times 10^8 \text{ s}^{-1}$  and  $U = 200 \text{ K}$ .

Thus Na in  $\text{KTaO}_3$  is, as well, a reorienting dipole defect. The comparison of experimental  $T_c(x)$  values with the theoretical formula [Eq. (3.2.3)] made possible an independent estimate of the amount of off-center displacement of Na, which amounted to approximately  $0.08 \text{ \AA}$  (Vugmeister and Glinchuk, 1979); this correlates fairly well with the NMR data.

Lanzi *et al.* (1987) observed a splitting of the soft-mode frequency, indicating a reduction in the symmetry of the low-temperature phase below  $T_c$ , but the magnitude of the splitting was considerably smaller than that for KTL, apparently because of the small value of the dipole moment of Na. As  $T_c$  was approached, the soft-mode frequency decreased, which indicated a displacement type of phase transition. However, these authors discussed the additional possibility that the splitting originated not in ferroelectric, but in structural domains where random antiparallel spontaneous polarization takes place. Such domains, in the opinion of these authors, would yield in Raman experiments the same effect as do domains with a homogeneous distribution of the polarization, but in dielectric experiments the crystal would exhibit dipole glass properties. Just such properties were observed by Maglione *et al.* (1986), who found a logarithmic frequency dependence of the imaginary part of the permittivity ( $\epsilon_2 \propto \omega^{\nu(T)}$ ), indicating the existence of a distribution of relaxation times, as for KTN and KTL. These authors also observed an increase in the nonlinear dielectric response, which they interpreted in terms of the spin-glass theory. However, as we have noted in Sec. IV B, for a correct analysis the critical increase in nonlinear susceptibility associated with the domain state must be separated from the true dipole-glass behavior. There is an ambiguity in Maglione *et al.*, (1986) separation of the ferroelectric domain contribution from full nonlinear susceptibility because the authors could not measure the static linear permittivity  $\epsilon(T)$  exactly. They could only calculate  $\epsilon(\omega \neq 0)$  by use of the Kramers-Kronig relation. With such treatment of the experimental data Maglione *et al.* (1986) did not obtain divergency of  $\epsilon(T)$  and therefore attributed all of the increase in  $\epsilon_{nl}$  to a dipole glass phase transition.

Höchli, Banfi, *et al.* (1989) reported on second-harmonic light generation and birefringence data in  $\text{KTaO}_3:\text{Na}$ . They calculated that a transition to a polar phase occurs at  $12 \text{ K}$ . The transition is characterized by an increase in the polar correlation length from  $300$  to  $1500 \text{ \AA}$  for  $15\%$  Na doping samples. The maximum correlation length is 2.5 orders of magnitude below that of a conventional ferroelectric and one order of magnitude above the spin-coherence length in  $\text{CuMn}$ . Thus it can be seen that  $\text{KTaO}_3:\text{Na}$  displays at certain concentrations more complex properties than those in dipole glasses and conventional ferroelectrics.

Ultrasonic investigation by Höchli, Doussineau, and Ziolkievich (1989) gave evidence of coherent tunneling of Na ions, within a correlation volume containing many impurities, through barriers with various heights and

asymmetry parameters. The tunneling was correlated with low-temperature phase formation (see also Torre and Rigamonti, 1987). The number of tunneling centers contributing to the sound velocity was about  $10^{-9}$  times the total number of Na ions in the crystal.

Thus the phenomena in the  $\text{KTaO}_3\text{:Na}$  system are on the whole quite similar to those in KTN and KTL.

## V. CONCLUSION

We have tried to acquaint the reader in adequate detail with the experimental work being done on the cooperative behavior of dipole impurities in dielectric crystals and to discuss the theoretical concepts underlying this field. The principal feature of such systems is spatial disorder in the arrangement of particles, due to which the observed properties differ greatly from the predictions of the mean self-consistent field theory. The main goal of this review was to show the relation between the form of the dipole-dipole interaction in dielectric crystals and the character of dipole ordering. To this end we looked first at  $\text{KCl:OH}^-$ ,  $\text{Li}^+$  as a pattern for a dipole impurity system in weakly polarizable dielectrics with the well-known form of a dipole-dipole interaction Hamiltonian. We then turned to the dipole-dipole interaction in highly polarizable crystals, where changes lead to the appearance of macroscopic ferroelectric domains, and the crystal as a whole displays the properties of ferroelectricity as well as of a dipole glass. However, as we saw in the experimental and theoretical part of this review, the experimental results are much richer and more complex than the simple theoretical notions presented here. Up to now, theory has not described in sufficient detail such phenomena as small domain size, competition between dipolar and quadrupolar ordering, and specificity of dynamic effects. Because of this discrepancy between theory and experiment it seems that internal static electric and elastic random fields as well as elastic quadrupolar interactions between impurities must play an important role in determining the physical properties of the system.

The systems under consideration are in many ways close to magnetic spin glasses, although they exhibit a certain specificity determined by the dipole-dipole interaction potential (in this sense they resemble dipole spin glasses). One of the most interesting unsolved problems in this field is the question of why the dipole forces in dilute systems do not lead to an equilibrium phase transition to the dipole glass state. A number of other unclear points exist regarding the comparison of  $\text{KCl:OH}^-$  dipole glass with magnetic spin glasses, in particular, why the long-time relaxation is well described within the framework of a simple pair interaction model without the need to allow for intercluster interaction. We hope that the present review will attract the attention of researchers to this problem.

A better understanding of systems containing off-center ions will probably be useful in studying the phenomena in magnetic spin glasses and in structural glasses,

where the situation is greatly complicated by the existence of different types of interactions. Of particular interest are investigations of highly polarizable crystals containing off-center ions, where a concentration phase transition from a dipole glass to a ferroelectric should occur at low temperatures. It is clear that near the critical concentration the system will exhibit anomalous properties differing from those of both a "classical" dipole glass and an ordinary ferroelectric.

So far, only the first steps have been taken both in theory and in experiment, and detailed analysis has been performed only in the random-field approximation. Moreover, no systems have as yet been found in which a concentrational phase transition could be induced experimentally by continuously increasing the concentration of dipoles. For  $\text{KTaO}_3\text{:Li}$ , for example, this is prevented by the need to use low temperatures (below 30 K) where, due to a higher barrier, thermal motion is completely frozen even for Li ions isolated from one another, so that no cooperative phenomena can be observed.

Therefore a purposeful search for new systems with off-center ions in highly polarizable crystals would be very desirable.

## NOTE ADDED

After this article was submitted for publication a number of papers appeared that have supplemented significantly the picture of the phenomena represented above.

(i) M. G. Stachiotti and R. L. Migoni [J. Phys. Condens. Matter, **2**, 4341 (1990)] applied the shell model to the calculation of lattice polarization near off-center Li ions in  $\text{KTaO}_3$ . Their results showed in particular that in highly polarizable crystals an effective dipole moment  $d^*$  of the off-center impurity does exceed significantly its proper dipole moment  $d$ , as follows from the macroscopic treatment presented in Sec. 111.A based on the Lorentz field model.

(ii) T. Nattermann, V. Shapir, and I. Vilfan [Phys. Rev. B **41**, 8577 (1990)] and T. Nattermann [Ferroelectrics **104**, 171 (1990)] investigated the effect on dynamic susceptibility of metastable domains induced by static random fields. According to these authors the existence of metastable domains results in a logarithmic dependence on the frequency of the dynamic susceptibility in  $\text{KTaO}_3\text{:Nb}$ ,  $\text{SrTiO}_3\text{:Ca}$ .

(iii) B. E. Vugmeister (to be published), using the random-field approximation developed above, has shown that an explanation for the very different critical concentration values of Li, Nb, and Na in  $\text{KTaO}_3$  can be given self-consistently if one assumes that they are caused by random static fields existing even in undoped  $\text{KTaO}_3$ . This finding allows us to understand why  $x_{\text{cr}}^{\text{Na}}$  is almost an order of magnitude higher than the critical concentration of Li and Nb, a fact that has been unexplained up until now.

(iv) Neutron scattering experiments in KTN with

$x^{Nb} \simeq 0.0012$  [H. Chou, S. M. Shapiro, K. B. Lyons, and D. Rytz, Phys. Rev. B **41**, 7231 (1990)] did not show any tetragonal distortions that could be seen as evidence of a ferroelectric phase transition. It seems to us the experiments can be understood if one takes into account the nonergodicity effects, which would be significant near critical concentrations  $x_{cr}^{Nb} \simeq 0.008$  where spontaneous polarization (long-range order) is less than the remanent polarization caused by clusters with short-range order.

(v) B. Recheav and Y. Yacoby (Proceedings of the W.EXAFS Conference at York, England, 1990) have made EXAFS studies of mixed perovskite systems. They managed to measure directly the local rotation of oxygen octahedra in  $K_{1-x}Na_xTaO_3$  as a function of  $x$ . The result suggests an antiferrodistorsive phase transition probably of the displacive type.

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**APPENDIX: TESTS OF THE RANDOM-FIELD METHOD ON MODEL SYSTEMS**

The random-local-field method, in the formulation used by us, relies on an exact formula [Eq. (2.11)],

$$L = \int dE f(E, L) l(E), \quad l(E) = \tanh \beta E, \quad (A1)$$

and on neglect of correlation effects in the orientations of different dipoles in calculating the function  $f(E)$ . To evaluate the degree of error brought about by such an approximation, a comparison with some model systems has been made (Vugmeister and Stefanovich, 1987b).

Let us compare, for example, the susceptibility and specific-heat values calculated by the random-field method for the Edwards-Anderson (1975) spin-glass model with corresponding values calculated by Binder and Stauffer (1976) and Soukoulis *et al.* (1983) by computer simulation. The Edwards-Anderson model is described by a Hamiltonian,

$$H = - \sum_{ij} J_{ij} l_i l_j, \quad l_i = \pm 1, \quad (A2)$$

and by a Gaussian distribution of  $J_{ij}$ , the interaction constant between  $z$  nearest neighbors. For such a model,  $F_2(\rho) = 0$ ;  $F_1(\rho) = \frac{1}{2} \rho^2 \Delta^2$ ;  $\Delta^2 = \sum_j J_{ij}^2 = zJ^2$ . The results of the calculation by Soukoulis *et al.* (1983) are shown in Fig. 30, along with the susceptibility and specific-heat values calculated by these authors and by Binder and Stauffer (1976) for a simple cubic lattice ( $z = 6$ ). It can be seen that the thermodynamic values, obtained by different methods agree well enough with one another, which serves as a certain test of the reasonableness of the random-local-field approximation. At the same time, the

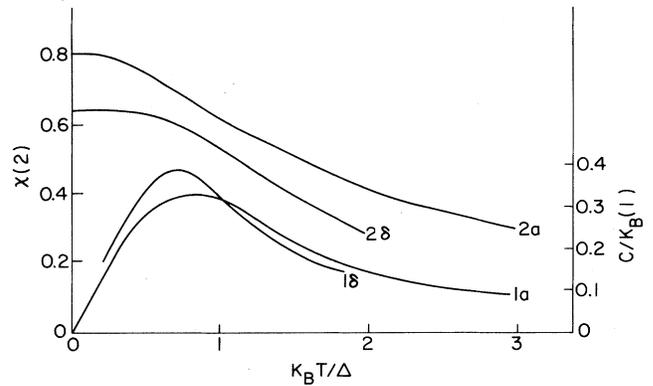


FIG. 30. (1) Susceptibility and (2) specific heat of spin glass according to the Edwards-Anderson model. Curves "a" were calculated by the random-field method (Vugmeister and Stefanovich, 1987b); curve 2a .

behavior of the susceptibility curves gives no indications of the existence of an equilibrium phase transition to the spin-glass state, which occurs in the system described by the Hamiltonian (A2). This discrepancy results from the limitations of the two approximations being compared. However, as has been noted in the principal text, experiments do not indicate the existence of an equilibrium phase transition in dipole glasses, and therefore the random-local-field method is particularly preferable for these systems.

let us consider also a model for the concentrational phase transition described by the Hamiltonian (A2), with

$$J = \begin{cases} +J_0, & r < r_c, \\ 0, & r > r_c. \end{cases} \quad (A3)$$

The value of the critical concentration for this model, calculated by the Monte Carlo method, satisfies the relation  $(4\pi/3)nr_c^3 = 2.7$  (Korenblit and Shender, 1978). Equation (A1) yields a value of  $(4\pi/3)nr_c^3 = 1.8$  (Vugmeister and Stefanovich, 1987a).

Let us now consider another, frequently encountered, model with the potential

$$J(r) = J_0 e^{-r/r_c}.$$

In such a system, in contrast to that above, the long-range order exists at any concentration of particles. The  $T_c(nr_c^3)$  values at  $nr_c^3 \ll 1$ , obtained from the percolation considerations, satisfy the relation (Korenblit and Shender, 1978)

$$T_c = J_0 \exp[-0.87(nr_c^3)^{-1/3}].$$

Equation (A1) yields a close value of the exponent: 0.62 instead of 0.87. Moreover, Eq. (A1) makes it possible to obtain the dependence  $T_c(nr_c^3)$  at any  $nr_c^3$  value and to pass continuously to the mean-field limit at high enough  $nr_c^3$  values (Vugmeister and Stefanovich, 1989, 1990).

We thus conclude that the random-local-field method

provides good qualitative accuracy for describing the thermodynamic characteristics of disordered systems.

## REFERENCES

- Abel, W. R., 1971, *Phys. Rev. B* **4**, 2696.
- Aharony, A., 1978, *Solid State Commun.* **28**, 667.
- Aminov, A. K., and B. I. Kochelaev, 1962, *Zh. Eksp. Teor. Fiz.* **42**, 1303 [*Sov. Phys. JETP* **15**, 903 (1962)].
- Andrews, S. R., 1985, *J. Phys. C* **18**, 1357.
- Antimirova, T. V., M. D. Glinchuk, A. P. Pechenyi, and I. M. Smolyaninov, 1990, *Fiz. Tverd. Tela* **32**, 208 [*Sov. Phys. Solid State* **32**, 116 (1990)].
- Axe, J., J. Harada, and G. Shirane, 1970, *Phys. Rev. B* **1**, 1227.
- Baranovskii, S. D., B. I. Shklovskii, and L. A. Efros, 1980, *Zh. Eksp. Teor. Fiz.* **78**, 395 [*Sov. Phys. JETP* **51**, 199 (1980)].
- Barker, A. S., and A. J. Sievers, 1975, *Rev. Mod. Phys.* **47**, 125.
- Bayer, N. E., and H. S. Sack, 1968, *J. Phys. Chem. Solids* **29**, 677.
- Bednorz, J. G., and K. A. Müller, 1984, *Phys. Rev. Lett.* **52**, 2289.
- Bersuker, I. B., 1971, *Structure and Properties of Coordination Compounds* (Khimiya, Leningrad).
- Binder, K., and D. Stauffer, 1976, *Phys. Lett. A* **57**, 177.
- Binder, K., and A. P. Young, 1986, *Rev. Mod. Phys.* **58**, 801.
- Boatner, L. A., U. R. Höchli, and H. E. Weibel, 1977, *Helv. Phys. Acta* **50**, 620.
- Born, M., and K. Huang, 1954, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford).
- Borsa, F., U. T. Höchli, J. J. van der Klink, and D. Rytz, 1980, *Phys. Rev. Lett.* **45**, 1884.
- Bray, A. J., and M. A. Moore, 1981, *J. Phys. C* **14**, 2629.
- Bridges, F., 1975, *Crit. Rev. Solid State Sci.* **5**, 1.
- Bruce, A. D., and R. A. Cowley, 1981, *Structural Phase Transitions* (Pion, London).
- Chase, L. L., E. Lee, and R. L. Prater, 1982, *Phys. Rev. B* **26**, 2759.
- Cornaz, P., U. T. Höchli, and H. E. Weibel, 1981, *Helv. Phys. Acta* **54**, 226.
- Courtens, E., 1981, *J. Phys. C* **14**, 37.
- Courtens, E., 1983, *Helv. Phys. Acta* **56**, 705.
- Courtens, E., 1985, *Jpn. J. Appl. Phys.* **24**, 70.
- Davis, T. G., 1972, *Phys. Rev. B* **5**, 2530.
- Dejgen, M. F., and M. D. Glinchuk, 1974, *Usp. Fiz. Nauk* **114**, 295 [*Sov. Phys. Usp.* **17**, 745 (1975)].
- de Almeida, J. R. L., and D. J. Thouless, 1978, *J. Phys. A* **11**, 983.
- de Yoreo, J. J., R. O. Pohl, J. C. La Sjaunias, and H. V. Löhenysen, 1984, *Solid State Commun.* **49**, 7.
- Dienes, G. L., R. D. Hatcher, R. Smoluchowski, and W. D. Wilson, 1966, *Phys. Rev. Lett.* **16**, 25.
- Edwards, S. W., and P. W. Anderson, 1975, *J. Phys. B* **5**, 965.
- Fiory, U. T., 1970, *Phys. Rev. B* **4**, 614.
- Fischer, B., and M. W. Klein, 1976, *Phys. Rev. Lett.* **37**, 756.
- Fischer, K. H., 1983, *Phys. Status Solidi B* **116**, 358.
- Fontana, M. D., W. Kress, G. Kugel, N. Lehner, and D. Rytz, 1984, *Ferroelectrics* **55**, 691.
- Gallen, H. B., 1961, *Solid State Commun.* **2**, 203.
- Geifman, I. N., A. A. Sytikov, V. I. Kolomytsev, and B. K. Krulikovskii, 1981, *Zh. Eksp. Teor. Fiz.* **80**, 2317 [*Sov. Phys. JETP* **53**, 1212 (1981)].
- Glinchuk, M. D., M. F. Dejgen, and A. A. Karmazin, 1973, *Fiz. Tverd. Tela* **15**, 2048 [*Sov. Phys. Solid State* **15**, 1365 (1973)].
- Glinchuk, M. D., A. A. Karmazin, and I. M. Smolyaninov, 1987, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **51**, 1697.
- Glinchuk, M. D., and I. M. Smolyaninov, 1988, *Fiz. Tverd. Tela* **30**, 1197 [*Sov. Phys. Solid State* **30**, 693 (1988)].
- Glinchuk, M. D., and I. M. Smolyaninov, 1990, *J. Phase Trans.* (in press).
- Halperin, B. I., and C. M. Varma, 1976, *Phys. Rev. B* **14**, 4030.
- Höchli, U. T., 1982, *Phys. Rev. Lett.* **48**, 1494.
- Höchli, U. T., and D. Baeriswyl, 1984, *J. Phys. C* **17**, 311.
- Höchli, U. T., G. P. Banfi, E. Giuotto, and G. Samoggia, 1989, *Europhys. Lett.* **9**, 729.
- Höchli, U. T., and L. A. Boatner, 1979, *Phys. Rev. B* **20**, 226.
- Höchli, U. T., P. Doussineau, and S. Ziolkievich, 1989, *Europhys. Lett.* **9**, 591.
- Höchli, U. T., P. Kofel, and M. Maglione, 1985, *Phys. Rev. B* **32**, 4546.
- Höchli, U. T., and M. Maglione, 1989, *J. Phys. Condens. Matter* **1**, 2241.
- Höchli, U. T., and A. Rigamonti, 1983, *J. Phys. C* **16**, 6321.
- Höchli, U. T., H. E. Weibel, and L. A. Boatner, 1978, *Phys. Rev. Lett.* **41**, 1440.
- Höchli, U. T., H. E. Weibel, and L. A. Boatner, 1979, *J. Phys. C* **12**, L563.
- Höchli, U. T., H. E. Weibel, and W. Rehwald, 1982, *J. Phys. C* **15**, 6129.
- Höck, K.-H., R. Schäfer, and H. Thomas, 1979, *Z. Phys. B* **36**, 151.
- Höck, K.-H., and H. Thomas, 1977, *Z. Phys. B* **27**, 267.
- Imbrie, J. Z., 1984, *Phys. Rev. Lett.* **53**, 1747.
- Imry, Y., and S. Ma, 1975, *Phys. Rev. Lett.* **35**, 1399.
- Imry, Y., and M. Wortis, 1979, *Phys. Rev. B* **19**, 3580.
- Kamitakahara, W. A., C. K. Loong, and E. S. Ostrowski, 1987, *Phys. Rev. B* **35**, 223.
- Känzig, W., H. R. Hart, and S. Roberts, 1964, *Phys. Rev. Lett.* **13**, 543.
- Kapchan, S., and F. Lüty, 1968, *Solid State Commun.* **6**, 907.
- Kind, R., and K. A. Müller, 1976, *Commun. Phys.* **1**, 223.
- Kirkpatrick, S., and C. M. Varma, 1978, *Solid State Commun.* **25**, 821.
- Kleeman, W., S. Kutz, and D. Rytz, 1987, *Europhys. Lett.* **4**, 239.
- Kleemann, W., S. Kutz, F. J. Schäfer, and D. Rytz, 1988, *Phys. Rev. B* **37**, 5856.
- Kleemann, W., F. J. Schäfer, K. A. Müller, and J. G. Bednorz, 1988, *Ferroelectrics* **60**, 297.
- Kleemann, W., F. J. Schäfer, and D. Rytz, 1985, *Phys. Rev. Lett.* **54**, 2038.
- Kleemann, W., H. Schremmer, and D. Rytz, 1989, *Phys. Rev. B* **40**, 7428.
- Klein, M. W., 1966, *Phys. Rev.* **141**, 489.
- Klein, M. W., 1989, *Phys. Rev. B* **40**, 1918.
- Klein, M. W., C. Held, and E. Zuroff, 1976, *Phys. Rev. B* **13**, 3576.
- Kopvillem, U. Kh., and R. V. Saburova, 1982, *Paraelectric Resonance* (Nauka, Moscow).
- Korenblit, I. Ya., and E. F. Shender, 1978, *Usp. Fiz. Nauk* **126**, 233 [*Sov. Phys. Usp.* **21**, 832 (1980)].
- Kristofel', N. N., 1979, *Fiz. Tverd. Tela* **21**, 895 [*Sov. Phys. Solid State* **21**, 523 (1979)].
- Kugel, G. E., M. D. Fontana, and W. Kress, 1987, *Phys. Rev. B* **35**, 813.
- Kugel, G. E., M. D. Fontana, H. Mesli, and D. Rytz, 1985, *Jpn. J. Appl. Phys.* **24**, 226.
- Kugel, G. E., H. Mesli, M. D. Fontana, and D. Rytz, 1988,

- Phys. Rev. B **37**, 5619.
- Kugel, G. E., H. Vogt, W. Kress, and D. Rytz, 1984, Phys. Rev. B **30**, 985.
- Lanzi, G., P. Milani, G. Samoggia, M. Maglione, and U. T. Höchli, 1987, Phys. Rev. B **36**, 1233.
- Lawless, W. N., 1966a, Phys. Kondens. Mater. **5**, 100.
- Lawless, W. N., 1966b, Phys. Rev. Lett. **17**, 1048.
- Lawless, W. N., R. W. Arenz, D. Rytz, and P. A. Buffat, 1985, Jpn. J. Appl. Phys. **24**, 263.
- Lawless, W. N., D. Rytz, and U. T. Höchli, 1981, Ferroelectrics **38**, 809.
- Lawless, W. N., D. Rytz, and U. T. Höchli, 1984, J. Phys. C **17**, 2609.
- Lee, E., L. L. Chase, and L. A. Boatner, 1985, Phys. Rev. B **31**, 1438.
- Lombardo, G., and R. O. Pohl, 1965, Phys. Rev. Lett. **15**, 291.
- Lüty, F., 1967, J. Phys. (Paris) Suppl. **28**, Colloque C-4, 120.
- Lyons, K. B., P. A. Fleury, T. J. Negran, and H. L. Carter, 1987, Phys. Rev. B **36**, 2465.
- Lyons, K. B., P. A. Fleury, and D. Rytz, 1986, Phys. Rev. Lett. **57**, 2207.
- Ma., S.-K. 1980, Phys. Rev. B **22**, 4484.
- Maglione, M., U. T. Höchli, and J. Joffrin, 1986, Phys. Rev. Lett. **57**, 436.
- Maglione, M., U. T. Höchli, J. Joffrin, and K. Knorr, 1989, J. Phys. Condens. Matter **1**, 1527.
- Maglione, M., S. Rod, and U. T. Höchli, 1987, Europhys. Lett. **4**, 631.
- Mahan, G. D., 1967, Phys. Rev. **153**, 983.
- Mahan, G. D., and R. M. Mazo, 1968, Phys. Rev. **175**, 1191.
- Manlief, S. K., and H. Y. Fan, 1972, Phys. Rev. B **5**, 4046.
- Medina, R., R. Nava, and M. Saint-Paul, 1984, Solid State Commun. **50**, 51.
- Migoni, R., H. Bilz, and D. Bäuerle, 1976, Phys. Rev. Lett. **37**, 1155.
- Moy, D., R. C. Potter, and A. C. Anderson, 1983, J. Low Temp. Phys. **52**, 115.
- Müller, K. A., 1985,
- Narayanamurti, V., and R. O. Pohl, 1970, Rev. Mod. Phys. **42**, 201.
- Oppermann, R., and H. Thomas, 1975, Z. Phys. B **22**, 387.
- Pechenyĭ, A. P., T. V. Antimirova, M. D. Glinchuk, and B. E. Vugmeister, 1988, Fiz. Tverd. Tela **30**, 1890.
- Peressini, P. P., J. P. Harrison, and R. O. Pohl, 1969, Phys. Rev. **180**, 926.
- Perry, C. H., and N. E. Tornberg, 1969, Phys. Rev. **183**, 595.
- Poplavko, Yu. M., V. P. Bovtun, and I. N. Geĭfman, 1983, Izv. Akad. Nauk SSSR, Ser. Fiz. **47**, 648 [Bull. Acad. Sci. USSR, Phys. Ser. **47**, 22 (1983)].
- Potter, R. C., and A. C. Anderson, 1981a, Phys. Rev. B **24**, 677.
- Potter, R. C., and A. C. Anderson, 1981b, Phys. Rev. B **24**, 4826.
- Prater, R. L., L. L. Chase, and L. A. Boatner, 1981a, Phys. Rev. B **23**, 221.
- Prater, R. L., L. L. Chase, and L. A. Boatner, 1981b, Phys. Rev. B **23**, 5904.
- Quigley, J., and T. R. Das, 1967, Phys. Rev. **164**, 1185.
- Quigley, J., and T. R. Das, 1969, Phys. Rev. **177**, 1340.
- Quigley, J., and T. R. Das, 1972, Bull. Am. Phys. Soc. **17**, 143.
- Reich, D. H., T. F. Rosenbaum, G. Aeppli, and H. J. Guggenheim, 1986, Phys. Rev. B **34**, 4956.
- Rigamonti, A., and S. Torre, 1986, Phys. Rev. B **33**, 2024.
- Rod, S., F. Borsa, and J. J. van der Klink, 1988, Phys. Rev. B **38**, 2267.
- Rytz, D., A. Chatelain, and U. T. Höchli, 1983, Phys. Rev. B **27**, 6830.
- Rytz, D., U. T. Höchli, and H. Bilz, 1980, Phys. Rev. B **22**, 359.
- Saint-Paul, M., and J. i. G. Gilchrist, 1986, J. Phys. C **19**, 2091.
- Saint-Paul, M., M. Mesa, and R. Nava, 1983, Solid State Commun. **47**, 183.
- Samara, G. A., 1984, Phys. Rev. Lett. **53**, 298.
- Samara, G. A., 1985, Jpn. J. Appl. Phys. **24**, 80.
- Schneider, T., H. Beck, and E. Stoll, 1976, Phys. Rev. B **13**, 1123.
- Schneider, T., and E. Pytte, 1977, Phys. Rev. B **15**, 1519.
- Schremmer, H., W. Kleemann, and D. Rytz, 1989, Phys. Rev. Lett. **62**, 1986.
- Sherrington, D., and S. Kirkpatrick, 1975, Phys. Rev. Lett. **32**, 1792.
- Slater, J. C., 1950, Phys. Rev. **78**, 748.
- Smolensky, G. A., E. G. Nadolinskay, N. K. Yushin, and A. V. Shilnikov, 1986, Ferroelectrics **69**, 275.
- Smolensky, G. A., A. V. Sotnikov, P. P. Syrnikov, and N. K. Yushin, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 30 [JETP Lett. **37**, 35 (1983)].
- Sommer, D., and W. Kleemann, 1990, Ferroelectrics (in press).
- Soukoulis, C. M., K. Levin, and G. S. Grest, 1983, Phys. Rev. B **28**, 1495.
- Strukov, B. A., E. L. Sorkin, N. K. Yushin, and S. A. Taraskin, 1986, Fiz. Tverd. Tela **28**, 3171 [Sov. Phys. Solid State **28**, 1785 (1986)].
- Tessmann, J. R., A. H. Kahn, and W. Shockley, 1953, Phys. Rev. **92**, 890.
- Thomsen, M., M. F. Thorpe, T. C. Choy, and D. Sherrington, 1984, Phys. Rev. B **30**, 250.
- Torre, S., 1987, Phys. Rev. B **36**, 803.
- Torre, S., and A. Rigamonti, 1987, Phys. Rev. B **36**, 8274.
- Triebwasser, S., 1959, Phys. Rev. **111**, 63.
- Uwe, H., K. B. Lyons, H. L. Carter, and P. A. Fleury, 1986, Phys. Rev. B **33**, 6436.
- Vaks, V. G., 1973, *Introduction to Microscopic Theory of Ferroelectrics* (Moscow).
- van der Klink, J. J., and F. Borsa, 1984, Phys. Rev. B **30**, 52.
- van der Klink, J. J., and S. N. Khanna, 1984, Phys. Rev. B **29**, 2415.
- van der Klink, J. J., S. Rod, and A. Chatelain, 1986, Phys. Rev. B **33**, 2084.
- van der Klink, J. J., and D. Rytz, 1983, Phys. Rev. B **27**, 4471.
- van der Klink, J. J., D. Rytz, F. Borsa, and U. T. Höchli, 1983, Phys. Rev. B **27**, 89.
- Vihnin, V. S., 1984, Fiz. Tverd. Tela **26**, 906 [Sov. Phys. Solid State **26**, 552 (1989)].
- Vihnin, V. S., and O. L. Orlov, 1983, Fiz. Tverd. Tela **25**, 41 [Sov. Phys. Solid State **25**, 22 (1983)].
- Vugmeister, B. E., 1984a, Fiz. Tverd. Tela **26**, 2448 [Sov. Phys. Solid State **26**, 1483 (1984)].
- Vugmeister, B. E., 1984b, Fiz. Tverd. Tela **26**, 1881 [Sov. Phys. Solid State **26**, 1141 (1984)].
- Vugmeister, B. E., 1985, Fiz. Tverd. Tela **27**, 1190 [Sov. Phys. Solid State **27**, 716 (1988)].
- Vugmeister, B. E., and T. V. Antimirova, 1990, Phys. Status Solidi **157**, 183.
- Vugmeister, B. E., and M. D. Glinchuk, 1979, Fiz. Tverd. Tela **21**, 1263 [Sov. Phys. Solid State **21**, 735 (1979)].
- Vugmeister, B. E., and M. D. Glinchuk, 1980, Zh. Eksp. Teor. Fiz. **79**, 947 [Sov. Phys. JETP **52**, 482 (1980)].
- Vugmeister, B. E., M. D. Glinchuk, and A. P. Pechenyĭ, 1984, Fiz. Tverd. Tela **26**, 3389 [Sov. Phys. Solid State **26**, 2036

- (1984)].
- Vugmeister, B. E., M. D. Glinchuk, and A. P. Pechenyĭ, 1989, *Fiz. Tverd. Tela* **31**, 158.
- Vugmeister, B. E., M. D. Glinchuk, A. P. Pechenyĭ, and B. K. Krulikowskii, 1982, *Zh. Eksp. Teor. Fiz.* **82**, 1347 [*Sov. Phys. JETP*, **55**, 783 (1982)].
- Vugmeister, B. E., V. V. Laguta, I. P. Bykov, and I. V. Kondakova, 1987, *Fiz. Tverd. Tela* **29**, 2449 [*Sov. Phys. Solid State* **29**, 1409 (1987)].
- Vugmeister, B. E., V. V. Laguta, I. P. Bykov, and I. V. Kondakova, 1989, *Fiz. Tverd. Tela* **31**, 54.
- Vugmeister, B. E., and V. A. Stefanovich, 1985, *Fiz. Tverd. Tela* **27**, 2034 [*Sov. Phys. Solid State* **27**, 1220 (1985)].
- Vugmeister, B. E., and V. A. Stefanovich, 1990, *Zh. Eksp. Teor. Fiz.* **97**, 1867.
- Vugmeister, B. E., and V. V. Stefanovich, 1987a, *Solid State Commun.* **67**, 323.
- Vugmeister, B. E., and V. V. Stefanovich, 1987b, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **51**, 2113.
- Vugmeister, B. E., and V. V. Stefanovich, 1988a, *Solid State Commun.* **66**, 673.
- Vugmeister, V. E., and V. V. Stefanovich, 1988b, *Fiz. Tverd. Tela* **30**, 1809 [*Sov. Phys. Solid State* **30**, 1039 (1988)].
- Wilson, W. D., R. D. Hatcher, G. L. Dienes, and R. Smoluchowski, 1967, *Phys. Rev.* **161**, 888.
- Yacoby, Y., 1978, *Z. Phys. B* **31**, 275.
- Yacoby, Y., 1981, *Z. Phys. B* **41**, 269.
- Yacoby, Y., A. Agranat, and I. Ohana, 1983, *Solid State Commun.* **45**, 757.
- Yacoby, Y., F. Cedeira, M. Schmidt, and W. B. Holzappel, 1975, *Solid State Commun.* **22**, 387.
- Yacoby, Y., W. B. Holzappel, and D. Bäuerle, 1977, *Solid State Commun.* **23**, 947.
- Yacoby, Y., and S. Just, 1974, *Solid State Commun.* **15**, 715.
- Zernic, W., 1965, *Phys. Rev.* **139**, 1010A.
- Zernic, W., 1967, *Phys. Rev.* **158**, 572.