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Ionic-thermocurrent study of the dipole relaxation and equilibrium in Gd-doped SrF_2†

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By means of thermal depolarization (ionic thermocurrent) measurements, the population of nearest-neighbor (type-I) and next-nearest-neighbor (type-II) Gd^{3+} interstitial fluoride ion dipoles have been observed as functions of temperature from 180 to 210 K, the region of the type-II dipole relaxation peak. The ratio of type-II to type-I concentration varies exponentially with reciprocal polarization temperature, indicating that at each temperature the two dipole species reach equilibrium within the polarization period, chosen to be at least six times the type-II dipole relaxation time. The enthalpy difference between the two species was determined to be 0.046 eV. The shift in the populations with temperature suggests that reorientation of the type-II dipole proceeds by means of the fluoride passing through a nearest-neighbor (type-I) site, in accordance with the accepted model. By assuming that the total number of dipoles remains constant, the ratio of the dipole moments of the two species is found to be 2.4.

I. INTRODUCTION

Because of Coulombic interaction, complexes tend to form between trivalent cation (M^{3+}) impurities, such as rare-earth ions, and their interstitial fluoride (F_i^-) charge compensators in oxygen-free alkaline-earth fluorides. The structure of these complexes have been studied by a variety of techniques in the fluorite crystals. Osiko,[1] as well as Fong and co-workers[2,3] have considered the relative populations of the various simple complexes from a chemical statistics viewpoint. However, for purposes of this paper we will consider only the two simplest dipolar complexes; namely type-I tetragonal (C_{4v}) dipoles with F_i^- located in a $\langle 100\rangle$ nearest-neighboring interstitial site to M^{3+} and type-II trigonal (C_{3v}) dipoles with F_i^- located in a $\langle 111\rangle$ next-nearest site as shown in Fig. 1. In CaF_2 the type-I structure is dominant as revealed by ESR[4-6] and electron-nuclear double resonance,[7-9] and optical spectra,[8,9] although a small amount of type II is indicated by fluorescence spectroscopy[10,11] and ionic thermoconductivity.[12] In BaF_2, the situation is reversed with type II dominating[13,14] and only a small concentration of type I suggested by ESR[12,15] and ITC[12] measurements. It is interesting that SrF_2, the intermediate member of this series, exhibits intermediate behavior[13,14]: both type-I and type-II dipoles are present in comparable quantities, though in SrF_2:Gd^{3+} type I is somewhat prevalent. The two dipoles in SrF_2:Gd^{3+} are manifested by thermal depolarization peaks with the following relaxation parameters[12]: The type-I peak lies at 143 K for a heating rate of 0.1 °K/sec and analysis by means of first-order relaxation yields a reorientation activation energy $E = 0.45$ eV and a reciprocal frequency factor $\tau_0 = 1\times10^{-14}$ sec. For the type-II dipole the peak lies at 206 K and $E = 0.62$ eV and $\tau_0 = 4\times10^{-14}$ sec.

The purpose of this paper is to describe our investigation of the equilibrium between type-I and type-II dipoles in SrF_2:Gd^{3+} and the mechanism by which this equilibrium is established. This work is part of a larger study of the equilibrium between dipolar species as well as the isolated M^{3+} and F_i^- components in the fluorite-structure alkaline-earth fluorides. This problem is important because of the anomalous concentration dependence of the distribution of M^{3+} over tetragonal and cubic sites observed by Franklin[16,17] in CaF_2. He also observed unusual effects of quenching from high temperature on the site distribution of M^{3+}. Although these observations do not directly involve type-II dipoles, these are a form intermediate between type I and the isolated components and it is to be expected that any anomalies would be reflected in their behavior as well. It is also important to verify the accepted relaxation model for type-II dipole reorientation which involves relaxation through nearest-neighbor (nn) type-I sites. Although we have also done work on CaF_2:M^{3+} crystals, the equilibrium situation in that system is indeed complex and is not yet clearly established. In contrast, the equilibrium behavior of dipoles in SrF_2:M^{3+} is quite consistent with the model. Therefore, only the SrF_2 results will be reported here and an account of the behavior of dipoles in CaF_2:M^{3+} will be treated in detail in a subsequent paper.

II. DIPOLE RELAXATION MODEL FOR THE FLUORITE STRUCTURE

The relaxation kinetics of $M^{3+} - F_i^-$ dipoles in the fluorite lattice and considerations of the relative stability of various dipole configurations have been recently reviewed by Lidiard.[18] The interstitial is considered as bound to the M^{3+} by Cou-

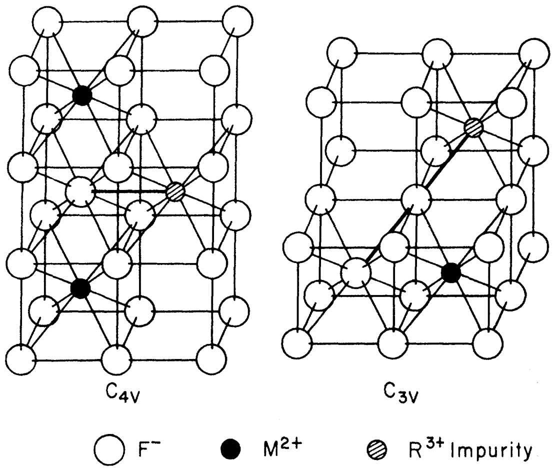

FIG. 1. C_{4v} (type-I) and C_{3v} (type-II) fluoride compensated dipolar complexes in MF_2:R^{3+}.

lombic and elastic interactions and the binding energy at various distances from the impurity is determined by charge interaction and lattice polarization. Fong and co-workers[3,19] have discussed the stability of the various configurations in some detail. Since there is no evidence of a contribution by dipoles of greater separation than next-nearest-neighbor (nnn) we shall confine our attention to nn and nnn dipoles. Reorientation of these dipoles is governed by the appropriate normal relaxation modes. These modes have been discussed by Franklin *et al.*[20] and by Nowick.[21] Perturbation of the orientational configuration by applied electric fields excites the triply-degenerate T_{1u} mode. The reciprocal relaxation time for this mode is two valued and is given by

$$\tau^{-1} = 2W_{11} + 2W_{12} + \tfrac{3}{2}W_{21} \pm [(2W_{11} + 2W_{12} - \tfrac{3}{2}W_{21})^2 + 4W_{12}W_{21}]^{1/2} \ . \qquad (1)$$

Here W_{ij}'s represent the frequency of interstitial transfer from site i to site j and subscript 1 refers to a nn site and site 2 refers to a nnn site. Figure 2 shows the interstitial sites in question connected by arrows indicating the direction of the W_{ij}'s. Because of structural considerations W_{22} is assumed to be zero. In addition the third-neighboring pair is considered to be so slightly bound that it is indistinguishable from the free components. In this model nnn or type-II dipoles reorient by movement through nn or type-I sites. Type-I sites however can reorient by a single W_{11}-type jump. When Coulomb interaction dominates, it is more difficult for the F_i^- to jump away than toward M^{3+}; hence it is expected that $W_{21} \gg W_{12}$. This implies that type-I dipoles have a greater

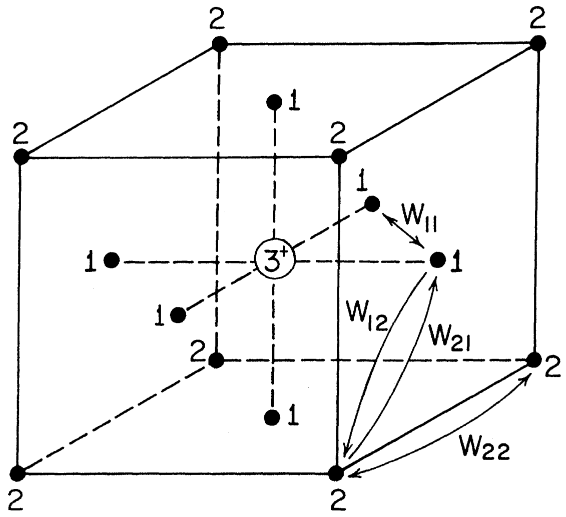

FIG. 2. Trivalent impurity ion and associated first and second neighbor fluoride interstitial sites. W_{ij} represents the probability per unit time of a jump of the interstitial fluoride from site i to site j.

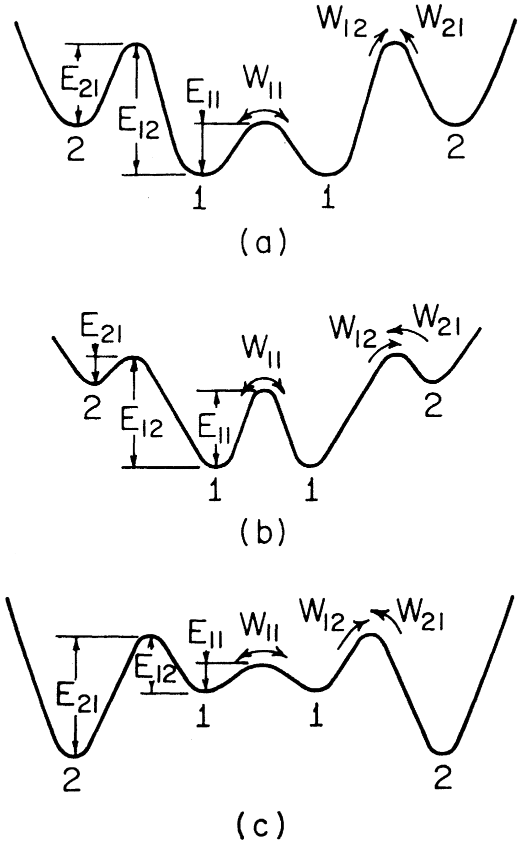

FIG. 3. Schematic energy representation of two type-I sites and two type-II sites with (a) $W_{11} \gg W_{21} \gg W_{12}$, (b) $W_{21} \gg W_{11} \gg W_{12}$, and (c) $W_{11} \gg W_{12} \gg W_{21}$.

stability than type-II dipoles as indeed is the case for $CaF_2:Gd^{3+}$ and $SrF_2:Gd^{3+}$. From ESR measurements[12,22] type-II dipoles are difficult to detect in $CaF_2:Gd^{3+}$ and are in the minority (1 to 4) in $SrF_2:Gd^{3+}$. Therefore, this relation between W_{21} and W_{11} is evidently correct for these compounds but not for $BaF_2:Gd^{3+}$ in which type II is dominant.

The saddle point configuration is shown in Fig. 3(a). This diagram is helpful in interpreting Eq. (1) physically since $W_{ij}=W_{ij}^0\exp(-E_{ij}/kt)$. The barrier E_{11} between equivalent configurations of type-I centers is shown to be lower than E_{12}, the barrier between type II and type I, which suggests that depolarization of type-I configurations can take place before and independent of type-II dipoles. It is of course possible that the type-II equilibration can occur before type I even though type-I dipoles are more stable: This latter situation is shown in Fig. 3(b). However, only one relaxation peak will be observed because the possibility of type-II relaxation via type-I sites erases the polarization of type-I dipole. The essential requirement for greater type-I stability is that $E_{12}\gg E_{21}$. For the case of interest to us here, namely, two relaxation peaks, the limiting solutions of Eq. (1) are

$$\tau_+^{-1}=4W_{11} \quad \text{and} \quad \tau_-^{-1}=3W_{21} \; , \tag{2}$$

provided only that $E_{11}<E_{12}$ and E_{21}. The situation in which type-II complexes are more stable than type I's but which still provides for two relaxation peaks as defined by Eq. (2) is shown in Fig. 3(c).

In principle, both relaxation times should be observable from ITC depolarization. For the situation shown in Fig. 2(a), type-I configurations mix freely at a temperature for which the type-II structure remains polarized. This relaxation corresponds to τ_+. A further increase in temperature is necessary before the type II reorients by converting from type II into type I and back into type II with a relaxation time of τ_-. In the situation represented by Fig. 3(b), however, type-II dipoles relax by τ_- at the lower temperature in interconverting with type-I dipoles. As a result, the imbalance between equivalent type-I configurations is erased before W_{11} jumps come into play. Therefore, one would expect the ITC peak associated with τ_+ to be weak if observable at all. Since two distinct ITC peaks are observed for $SrF_2:M^{3+}$, these considerations suggest that the situation of Fig. 2(a) applies.

In the above discussion it is evident that the W_{12} and W_{21} jumps lead to equilibrium between the type-I and type-II structures. Equilibrium occurs when

$$4N_IW_{12}=3N_{II}W_{21} \; , \tag{3}$$

in which N_I and N_{II} represent the dipole concentrations in the two configurations the numerical factors indicate the number of sites into which an F_i^- can jump which transform the dipole from one type into another. From Eq. (3) the ratio between the concentration of the two dipole types is

$$\frac{N_{II}}{N_I}=\frac{4W_{12}}{3W_{21}}=\exp\left(\frac{\Delta S_{12}}{k}-\frac{\Delta E_{12}}{kT}\right), \tag{4}$$

where the entropy difference between the two types $\Delta S_{12}=\ln(4W_{12}^0/3W_{21}^0)$ and the enthalpy difference $\Delta E_{12}=E_{12}-E_{21}$.

For this situation it is evident from Fig. 2(a) that thermal reorientation of type-II dipoles involves the interchange between the two forms necessary to establish equilibrium. Therefore, equilibration at various temperatures across the type-II ITC peak should produce a variation in N_{II}/N_I as predicted by Eq. (4). The actual populations can of course be obtained from the areas under each peak exhibited by the subsequent thermal depolarization run provided the dipole moments of each type of dipole is known since

$$P=\mu^2N_d\,E_p/3kT_p \; , \tag{5}$$

where the saturation polarization P is given by the area under the peak, μ is the dipole moment, N_d is the dipole concentration, and E_p and T_p are the polarizing field and temperature of polarization, respectively. Hence, it should be possible to obtain ΔE_{12} from the slope of a semilog plot of the dipole ratio versus reciprocal temperature and ΔS_{12} from the intercept at $1/T=0$.

Conservation of the total number of dipoles should also hold since only interconversion from one type to the other is expected during the equilibration process. In principle, this provides a means of determining the ratio of dipole moments, namely,

$$N_I+N_{II}=N_T=\frac{3k}{E_p\mu_I^2}\left(P_IT_{PI}+\frac{\mu_I^2}{\mu_{II}^2}P_{II}T_{P_{II}}\right). \tag{6}$$

In order for such a method to be truly effective in evaluation of dipole moment ratios the variation of N_I and N_{II} over the thermal range chosen for equilibration must be sizable. Even for small variations, however, it should be possible to make a rough check of Eq. (6) using the unrelaxed point ion (UPI) values of the dipole moments.

Finally, it should be pointed out that neither Eq. (4) and (5) will apply if there is an alternative relaxation path for type-II dipoles which has a lower saddle point than E_{21}. Thus far we have made no mention of the actual atomic motions required to accomplish the reorientations in question. Dipole reorientation could be accomplished by either interstitial jumping or by interstitialcy transfer. Our only assumption for the above discussion is that the W_{22} is zero. Consideration of alternate paths for type-II reorientation makes it necessary to evaluate the actual jump mechanism. Catlow[23] has done this taking into account relaxation of the positions of lattice ions around the F_i^- and M^{3+}. The results are interesting in that, whereas previously the interstitialcy (replacement) jump was considered to be much more probable than the interstitial (direct) jump, he finds both direct interstitial jumps and interstitialcy jumps not very different in activation energy. Moreover, a relatively low-energy nnn → nnn interstitialcy jump is postulated which involves a common saddle point with a direct nn → nn jump but which does not require that the nn site actually be used in type-II reorientation. The alternate path is especially favorable for BaF_2 but less likely for CaF_2 and SrF_2. Nevertheless, this possibility weakens the customary assumption that W_{22} is zero and opens up the prospect that relaxation of type-II dipoles can occur independently of type I and that the two types do not necessarily have to be in equilibrium at the temperature of the type-II ITC peak.

III. EXPERIMENTAL DETAILS

The primary experimental tool used in this study is ITC or thermal depolarization, first employed by Bucci *et al.*,[24,25] which provides a sensitive measure of the kinetic parameters involved in dipole reorientation as well as the concentration of dipolar defects. In essence, ITC involves (i) polarization of the sample by application of an electric field at a temperature for which the dipole relaxation time τ is short, (ii) freezing in this preferred dipolar orientation by cooling rapidly with the polarizing field still applied to a temperature for which τ is long compared to the duration of the experiment, and (iii) depolarization by warming at a linear heating rate with the field removed. During step (iii) the displacement current I_d associated with depolarization is monitored as a function of temperature. A peak in I_d occurs in the temperature range over which a set of dipoles reorients. From the shape and position of the ITC peak the activation energy E and reciprocal frequency factor τ_0 can be obtained using first-order reorientation kinetics by methods described earlier.

The SrF_2 crystals used in this study were obtained from Optovac, Inc. in the form of 10-mm-diam rods with a nominal doping of 0.1-mole% Gd. Individual specimens up to 1 mm thick were cleaved from the rod and powdered silver electrodes were painted on each surface. The specimens were mounted in a high impedance chamber in a nitrogen cryostat. The polarizing fields were ~5000 V/cm. Currents were measured using a Cary 401 vibrating-reed electrometer. The peak heights measured were of the order of 10^{-12} A with a background noise level of ~10^{-15} A. The heating rates were 3 K min^{-1} through the type-I peak and 5 °K min^{-1} through the type-II peak. Linear heating rates were obtained by monitoring the emf of a copper-constantan thermocouple, and nulling this against a reference voltage generated by an on line PDP-12 computer according to a second degree polynomial approximation to the thermocouple emf-vs-T curve. The imbalance signal controlled the specimen heater current. The specimen chamber was filled with 1-atm helium exchange gas to minimize temperature gradients across the specimen.

To test the validity of the model as described in Eq. (4), the temperature dependence of the ratio N_{II}/N_I was determined by the following procedure: The specimen was "annealed" in the polarizing field at a temperature in the range spanning the type-II ITC peak for a period equal to or greater than six type-II relaxation times. It was then cooled rapidly under applied field to a temperature near the type-I peak, held there for a short time and then cooled further to immobilize the type-I dipoles. The ITC run was then carried out in the usual way. The procedure was then repeated for other "anneal" temperatures until the range was covered. The "anneal" accomplishes two purposes: (i) it permits polarization of type-II dipoles to saturation and (ii) it allows equilibrium to be established between type I and type II. It was necessary to confine the experiment to the range 185–215 K. At temperatures lower than this the annealing period becomes prohibitively long already amounting to ~15 h at 185 K. At higher temperatures, the available quench rate is not sufficient to quench in the established equilibrium ratio or polarization. The pause in cooling near the type-I peak is necessary to establish a definite polarization temperature for this set of dipoles as well.

IV. RESULTS AND DISCUSSION

From the areas under the type-I and type-II peaks it is possible by means of Eq. (5) to calculate the dipole concentrations and hence N_{II}/N_I, provided the correct values of μ_I and μ_{II} are known. In previous work,[12] the unrelaxed point-ion (UPI) dipole moments were used in estimates of dipole concentrations: this requires $\mu_I = \frac{1}{2}ea_0$ and $\mu_{II} = \frac{1}{2}(\sqrt{3}\,ea_0)$, where e is the electron charge and a_0

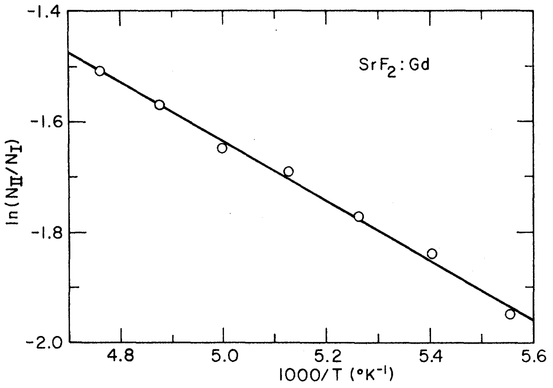

FIG. 4. Ln (N_{II}/N_I) vs $1000/T$, where T is the temperature of polarization, as determined by thermal depolarization measurements. UPI dipole moments were assumed. The slope of the line corresponds to $\Delta E_{12} = 0.046$ eV, and the intercept to $\Delta S_{12} = 1.0k$.

is the lattice constant. These values of the μ's were assumed in calculating the N_{II}/N_I temperature dependence which is shown in Fig. 4. The observed ratio varies from 0.14 at 185 K to 0.22 at 215 K. The solid line shows the best straight-line fit to the data. The fit is excellent with a 1% standard deviation in the ratio, a value roughly equivalent to the overall experimental error in the ITC measurement. The slope of the line corresponds to $\Delta E_{12} = 0.046$ eV and the intercept yields a value of $1.0k$ for ΔS_{12} which seems to be reasonable. These results strongly support the accepted model for equilibrium and interconversion of type-I and type-II dipolar complexes in SrF_2.

It should be pointed out that whereas an error in choice of values for the dipole moments would have no effect on the value of ΔE_{12}, it would certainly affect ΔS_{12} which depends upon the absolute magnitude of N_{II}/N_I. To examine the reasonableness of the UPI values, the test offered by Eq. (6) was employed. The ratio μ_{II}/μ_I required to give the best match to the condition $N_I + N_{II} = N_T$ was found to be 2.4, a value 40% larger than the UPI value used in constructing Fig. 3. Although this new ratio seems unusually large, recent studies by Sherstkov *et al.*[26] tend to support it. From a study of the effect of an electric field upon the ESR of CaF_2:Gd^{3+} they found that μ_I is 0.77 of the UPI value, suggesting a strong inward relaxation as well as a possible shift in the charge distribution around the dipole. In SrF_2, with the larger ionic radius of Sr^{2+} (1.13 Å) as compared to Ca^{2+} (0.99 Å), one might expect the small size of the impurity ion (0.94 Å for Gd^{3+}) to cause an even greater reduction in μ_I. In addition, it seems reasonable that the relaxation in the type-II dipole would be less than in the case of the type I because the components are more remote from each other. If this is indeed the case, the large difference between the dipole moment ratio estimated from the data and the UPI value is not unreasonable. These results also indicate that $\Delta S_{12} = -0.04k$, rather that the larger value given above.

Similar studies have been carried out on CaF_2:Gd^{3+} but the results are quite different. The ratio N_{II}/N_I showed very little temperature dependence for equilibration over the temperature range 197–225 K spanning the type-II ITC peak. This behavior suggests that the dipoles responsible for the type-I and type-II peaks reorient independently of one another, a possibility supported by the fact that ^{137}Cs γ irradiation near room temperature decreases the type-II dipole density by 36%, whereas the type-I concentration decreases only 7.5% as estimated using the UPI dipole moments. The dipole destruction presumably comes about by electron capture by the Gd^{3+} ion. However, if the two forms were in equilibrium at the temperature of the type-II peak (221 K) the ratio of concentration should be unaffected. This behavior suggests that either the two dipolar species are not in equilibrium below room temperature, the type-II dipoles are relaxing by an alternative path as discussed by Catlow,[23] or the upper peak is not associated with type-II dipoles but with some other species. These results will be the subject of a subsequent paper.

V. CONCLUSIONS

From the studies of the thermal equilibrium between and the relaxation behavior of type-I and type-II dipoles in SrF_2:Gd^{3+} we conclude that the accepted model for these dipoles in the fluorite structure is substantially correct. The temperature dependence of the ratio N_{II}/N_I yields an enthalpy difference $\Delta E_{12} = 0.046$ eV. Applying the conservation condition leads to a ratio of dipole moments $\mu_{II}/\mu_I = 2.4$. This is consistent with an entropy change between the two forms which is near zero.

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[1] V. V. Osiko, Sov. Phys.-Solid State 7, 1047 (1965).

[2] F. K. Fong and M. A. Hiller, J. Phys. Chem. 71, 2854 (1967).

[3] R. H. Heist and F. K. Fong, Phys. Rev. B 1, 4240 (1970).

[4] B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. B 69, 858 (1956).

[5] J. M. Baker, W. Hayes, and M. C. M. O'Brien, Proc. R. Soc. A 254, 273 (1960).

[6] M. J. Weber and R. W. Bierig, Phys. Rev. 134, A1492 (1964).

[7] J. M. Baker, E. R. Davies, and J. P. Hurrell, Phys. Lett. A 26, 352 (1968).

[8] D. Kiro and W. Low, in *Magnetic Resonance*, edited by C. K. Coogun, N. S. Ham, S. N. Stuart, J. R. Philbrow, and G. V. H. Wilson (Plenum, New York, 1970), p. 247.

[9] E. Secemski, D. Kiro, W. Low, and D. J. Schipper, Phys. Lett. 45, 6 (1970).

[10] J. B. Fenn, J. C. Wright, and F. K. Fong, J. Chem. Phys. 59, 5591 (1973).

[11] D. R. Tallant and J. C. Wright, J. Chem. Phys. 63, 2079 (1975).

[12] E. L. Kitts, M. Ikeya, and J. H. Crawford, Phys. Rev. B 8, 5840 (1974).

[13] J. Sierro, Phys. Lett. 4, 178 (1963).

[14] U. Ranon and A. Yanio, Phys. Lett. 9, 17 (1964).

[15] A. Kiel and W. B. Mims, Phys. Rev. B 6, 34 (1972).

[16] A. D. Franklin and S. Margullo, Proc. Brit. Ceram. Soc. 19, 135 (1971).

[17] A. D. Franklin, J. Non Met. 1, 27 (1972).

[18] A. B. Lidiard, in *Crystals with the Fluorite Structure*, edited by W. Hayes (Oxford U.P., London, 1974), Chap. 3.

[19] F. K. Fong, R. L. Ford, and R. H. Hirst, Phys. Rev. B 2, 4202 (1970).

[20] A. D. Franklin, A. Shorb, and J. B. Wachtman, J. Res. NBS 68A, 425 (1964).

[21] A. S. Nowick, Adv. Phys. 16, 1 (1967); J. Phys. Chem. Solids 31, 1819 (1970).

[22] C. -C. Yang, S. Lee, and A. J. Bevolo, Phys. Rev. B 13, 2762 (1976).

[23] C. R. A. Catlow, J. Phys. C 9, 1845 (1976).

[24] C. Bucci and R. Fieschi, Phys. Rev. Lett. 12, 16 (1964).

[25] C. Bucci, R. Fieschi, and G. Gaidi, Phys. Rev. 148, 816 (1966).

[26] Yu. A. Sherstkov, V. A. Yazhenin, and K. M. Zolotareva, Sov. Phys.-Solid State 17, 1828 (1976).