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Condensation of Random-Site Electric Dipoles: Li in KTaO$_3$

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Nuclear magnetic resonance and dielectric susceptibility data are reported in KTaO$_3$:Li which show, for the first time, ordering of random-site electric dipoles in a nonpolar lattice.

Intensive research has been recently conducted on randomly interacting (or random-site) dipoles with the aim of understanding the nature of their condensed state. The question still appears to be open even as to its very existence, both from an experimental and theoretical point of view.[1] Most of the work has been on magnetic systems whose condensed state (if it exists) is called spin glass. It has been less appreciated that randomly interacting electric dipoles have also been predicted to condense.[2] Such condensation, i.e., the presence of an electric-dipole glass has also been hypothesized on the basis of observed electret polarization.[3] The close analogy of the two systems and the availability of a well-behaved random electric-dipole system led us to search

for the analog of a spin glass.

Thus, for the first time, we provide experimental evidence for condensation of random-site interacting electric dipoles. To this end, we study the dipole moment arising from the off-center position of Li$^+$ replacing K$^+$ in KTaO$_3$. The local sites of Li$^+$ in the lattice are determined by nuclear magnetic resonance (NMR), whereas the global behavior of interacting dipoles is probed by dielectric measurements.

KTaO$_3$ turns out to be a most suitable lattice to host an electric dipole, Li$^+$, whose infrared properties have been explored[4] and whose giant single-particle response[5] had been related to the large susceptibility of the lattice.[6] Furthermore, the relevant Li relaxation and the concommittant

dielectric dispersion are found in the convenient kHz range.

The low-temperature, $T < 50$ K, NMR spectrum of ^{7}Li in $K_{1-c}Li_cTaO_3$ consists of seven lines for a general orientation of the crystal with respect to the magnetic field. The angular dependence of the spectrum shows unambiguously that the Li ions are off center and evenly distributed among six well-defined equivalent positions along the fourfold cube axes. The components of the local electric-field gradient (EFG) tensor have the same magnitude at all sites but directions different by an angle $\frac{1}{2}\pi$. A value of $\nu_Q = e^2qQ/2h = 70 \pm 2$ kHz is found, independently of c or T. In an ionic charge approximation[7] this leads to a displacement of the Li$^+$ ion of 0.86 Å.

At higher temperatures, $T > 50$ K, the NMR spectrum of ^{7}Li consists of a single isotropic and symmetric line indicating a zero time average of the EFG tensor. In this range, the nuclear-spin relaxation rate T_1^{-1} depends on temperature[8] through the correlation time τ_c as

$$\frac{1}{T_1} = \frac{(4\pi\nu_Q)^2}{50}\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right). \quad (1)$$

Equation (1) has been derived for $\frac{1}{2}\pi$ jumps of Li

FIG. 1. NMR and dielectric relaxation data, and Li hopping rate τ^{-1} derived therefrom by Eqs. (2) and (3). Full lines and left-hand scale: fit to Eq. (1) of the points marked by crosses and pluses. Dashed line and right-hand scale: Eq. (2) derived from this fit. The points marked by squares are well represented by this line, showing that Li hopping is the cause of both NMR and dielectric relaxation.

between the sites found from the low-temperature spectrum at a rate

$$\tau^{-1} = (6\tau_c)^{-1} = \tau_0^{-1}\exp(-E/kT). \quad (2)$$

Experimental data for several different crystals are shown in Fig. 1 together with a simultaneous fit to NMR data at two frequencies and to dielectric data (see below) for $c = 0.009$. The parameters of the fit are $E = 1000$ K and $\ln\tau_0 = -29.66$. Parameters obtained at other values of c are the same to within $\pm 10\%$, which show that the local properties of Li ions in $KTaO_3$ are unaffected by the presence of other Li ions as long as $c < 0.07$.

To probe the collective properties of the Li dipoles, the complex dielectric susceptibility $\chi = \chi' + i\chi''$ was measured at different frequencies. It may be represented[9] in terms of the convolution of relaxation functions

$$\chi = \chi_1 + \chi_2\int p(\tau_d)d\tau_d/(1+i\omega\tau_d)$$

with a log-normal probability distribution $p(\tau_d)$. At a frequency $\omega_m = \langle\tau_d^{-1}\rangle$, where $\langle\tau_d\rangle$ is the most probable relaxation time, a maximum of χ'' is found, allowing a determination of the hopping rate τ^{-1} from

$$\tau^{-1} = \frac{1}{2}\langle\tau_d^{-1}\rangle = \frac{1}{2}\omega_m. \quad (3)$$

Values of τ^{-1} determined this way for two crystals have also been plotted in Fig. 1, where the dashed line represents Eq. (2) with the above-mentioned values of E and $\ln\tau_0$. The agreement between τ values derived from NMR and from dielectric data shows that the dielectric relaxation is due to the hopping motion of the Li ions.

For frequencies large compared to the hopping rate, $\omega^+ \gg \tau^{-1}$, the susceptibility $\chi(\omega^+) = \chi_1$ is due to the lattice polarizability only, whereas for $\omega^- \ll \tau_c^{-1}$, the Li can follow the slowly varying field and also contribute to the total polarizability. The dielectric dispersion step $\chi(\omega^-) - \chi(\omega^+) = \chi_2 = \chi_{Li}$ is thus a measure of the polarizability of the Li subsystem only. The important experimental fact is that χ_{Li} shows maxima both as a function of temperature T and of Li concentration c. First, typical experimental χ_{Li} vs T data at a particular value of c, both without and with a biasing dc field, are given in Fig. 2. The cusplike peak, which is effectively quenched by the dc field, indicates an "ordering." But at temperatures below those corresponding to χ_{Li}^{max} no spontaneous bulk polarization is observed, nor can a permanent polarization be induced by application of a dc field, regardless of its strength[3]; instead in this temperature region, and only here, electret po-
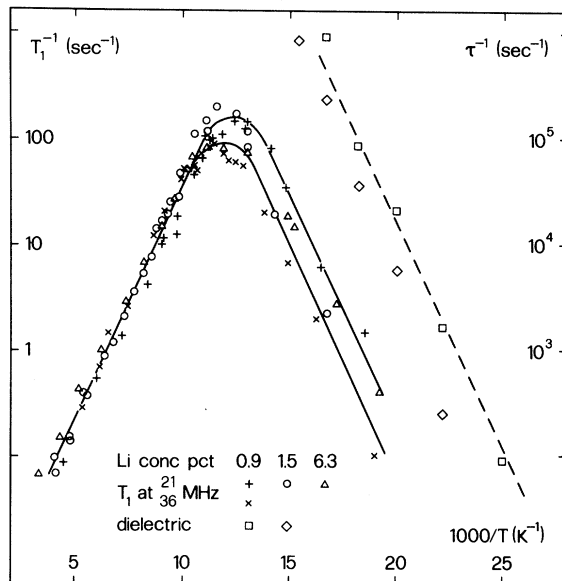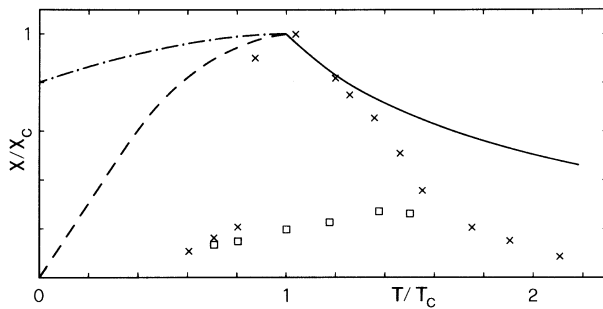
FIG. 2. Temperature dependence of χ_{Li} at $E = 0$ (crosses) and at $E = 2 \times 10^5$ V/m (squares). $c = 0.04$. Full curve, susceptibility according to Refs. 2, 12, and 13; dashed curve, Ref. 12; and dash-dotted curve, Ref. 13.
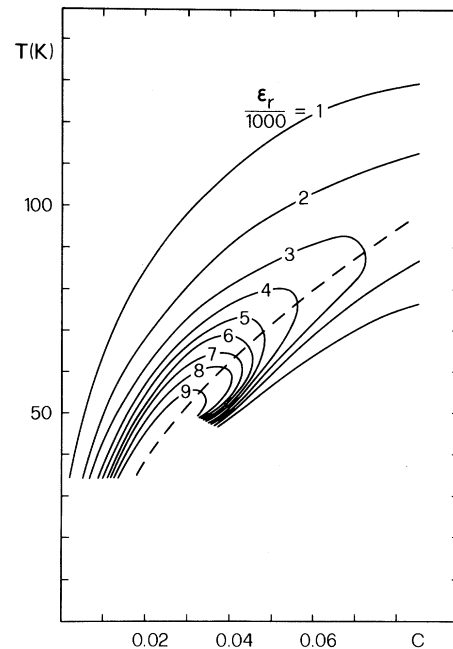

FIG. 3. Dielectric dispersion of Li dipoles. Contours of constant $\epsilon_r/1000$ are drawn on the c-T plane. Dashed line: the phase diagram according to Ref. 2 (for two-orientational dipoles) $T_c \sim c^{0.66}$.

larization and optical birefringence[10] appear. Such findings are typical of condensation and atypical of single-particle freezing in a matrix.[6] The data are, therefore, now discussed in the light of investigations on collective ordering in random systems.

In Ref. 2, the mean–random–molecular-field (MRF) approximation has been used to describe the behavior of a system of randomly distributed tunneling dipoles. A phase transition was predicted to occur if the first moment of the dipole field distribution at zero temperature, $\eta_1(0)$, is greater than the tunneling matrix element δ. Under the assumptions $\delta \ll \eta_1(0)$ and $\delta \ll kT$, some of the results of Ref. 2 are as follows:

(i) There is a minimum concentration c_0 of dipoles needed for "ordering" to occur;

(ii) the phase diagram is given by $T_c \sim c^\alpha$ with $\alpha < 1$ (and $\alpha = 0.66$ in an intermediate concentration range for a specific model considered);

(iii) the high-temperature susceptibility is of the simple Curie-type, there is a cusp in the $\chi(T)$ relation at T_c which should be suppressed by an electric field.

These predictions are now tested in turn.

Our data for $K_{1-c} Li_c TaO_3$ indicate a limiting concentration $0.6 \times 10^{-2} < c_0 < 1.6 \times 10^{-2}$ for order to occur. By analogy with $K_{1-c} Li_c Cl$ where broadening of paraelectric resonance lines at $c \sim 10^{-5}$ indicates the onset[11] of collective "disorder," and by assuming the two lattices to be identical except for their susceptibility ($\chi_{KCl}/\chi_{KTaO_3} \sim 10^{-3}$), we conclude $c_0 \sim 10^{-2}$, in crude agreement with observations. Next, the proposed phase diagram of Ref. 2 is drawn in Fig. 3, where the full lines are smoothed experimental contours of χ_{Li} in the c-T plane. It is seen that the predicted phase

boundary coincides closely with the experimentally determined locus of maximum χ_{Li}. Finally, as shown in Fig. 2, the predicted cusp in the $\chi(T)$ relation and its quenching by an electric field are qualitatively confirmed by experimental observations. The agreement remains qualitative, however: Above T_c, the predictions which are identical for magnetic and electric moments, indicate Curie behavior. They underestimate the steepness of the cusp. Below T_c explicit theoretical results are available only for spin systems, the one derived from self-consistent mean field theory[12] shows a definite, although not ultimate, improvement over the one derived from the replica method[13] (see Fig. 2).

The essential experimental features of $K_{1-c} Li_c TaO_3$ are thus explained in terms of a mean-field theory taking into account randomly interacting dipole moments. Remaining discrepancies may be attributed to a breakdown of mean-field theory predicted to occur in six dimensions.[14] As test materials for random-field theories, electric dipole glasses such as $K_{1-c} Li_c TaO_3$ may be superior to spin glasses since the lattice susceptibility can be separated from the dipolar susceptibility by measuring the frequency-dependent response. The procedure avoids subtracting a back-

ground of complex (electronic) origin.

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Random Dilution at Marginal Dimensionality in $LiTb_pY_{1-p}F_4$

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The $T_c(p)$ vs p phase diagram and the critical behavior of the magnetic susceptibility of the randomly diluted, three-dimensional, Ising, dipolar-coupled ferromagnet $LiTb_pY_{1-p}F_4$ has been measured for $0.97 \geqslant p \geqslant 0.46$. For $p \geqslant 0.46$ the $T_c(p)$ phase diagram obeys the relation $T_c(p) = 2.88 \text{ K} - (3.24 \pm 0.10 \text{ K})(1-p)$. At small p, a power-law fit is found to be qualitatively more in agreement with the data than either the renormalization-group logarithmically corrected power law or a recent prediction for the random dipolar Ising magnet.

Recently there has been considerable interest in the critical phenomena of randomly diluted magnetic materials. According to a heuristic argument by Harris,[1] as well as subsequent renormalization-group (RG) calculations,[2] one should expect a crossover to a new type of critical behavior in a random magnetic material if the specific heat in the nonrandom magnetic material diverges at the transition temperature. In this case there will be a crossover to a new fixed point with new critical point exponents. One of the few cases known to exhibit a divergent specific heat is the Ising $(n=1)$, three-dimensional $(d=3)$ magnet. A second area of critical phenomena in which there has been much theoretical and experimental activ-

ity is the concept of marginal dimensionality d^*. At $d=d^*$ the RG recursion relations can be solved "exactly" without the necessity of ϵ or $1/n$ expansions for the critical-point exponents. Experiments at this dimensionality offer the most stringent test of theoretical predictions. The marginal dimensionality d^* depends on the details of the magnetic interaction. In magnetic systems, experimentally accessible values of d^* only occur at the tricritical point in uniaxial antiferromagnets and at the critical point of three-dimensional, dipolar-coupled, Ising ferromagnets.[3] Therefore, in the randomly diluted, three-dimensional, Ising, dipolar-coupled ferromagnets, in which there have been few measurements, the effects of both