Cooperative phenomena in crystals containing off-center ions—dipole glass and ferroelectricity

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The current state of experimental and theoretical research into cooperative phenomena in crystals containing off-center ions is reviewed. This field has attracted considerable attention in recent years because of the general interest in disordered systems, including spin glasses of which dipole glass is the electric analog. The properties of dipole glass in alkali halide crystals containing off-center ions are discussed. Experimental studies performed over the last few years have shown that off-center ions can induce the ferroelectric phase transition in highly-polarizable crystals. The physical nature and the theory of the phenomenon are examined, and the physical properties of crystals exhibiting this induced phase transition are discussed. Possible lines of future research into cooperative phenomena in crystals containing off-center ions are reviewed.

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1. INTRODUCTION

Although it has a long history, going right back to the work of Langevin and Debye, the problem of dipolar-particle ordering is still of current interest today. This is particularly true of impurity-containing systems which are highly sensitive to "spatial disorder," i.e., the randomly irregular disposition of impurities. Thus, according to the Langevin-Debye theory in which the interaction between particles is described in terms of an effective self-consistent field (the Lorentz field in the case of dipole systems), a "polarization catastrophe" should occur as the temperature is reduced, i.e., the polarizability of the system should increase without limit and give rise to ferroelectric instability.

However, even early experiments[1–3] with alkali halide crystals containing dipole impurities showed that nothing like this actually happens, and the ferroelectric phase transition does not occur. This can be explained in terms of the specificity of the dipole-dipole interaction potential. Both the magnitude and sign of the interaction are very dependent on the relative orientations of the dipoles and on their positions. This in turn leads to a considerable spread in the local fields that are produced by impurities and act on different dipoles in impurity-containing systems, so that the homogeneous self-consistent field ceases to be a valid approximation. And although attempts were made in early theoretical work[4,5] to describe the experimental results without taking into account spatial particle fluctuations, but using different variants of the self-consistent field, it became clear in the course of subsequent analyses[6–8] that such fluctuations substantially reduce the effective polarizability and therefore prevent the onset of ferroelectric instability.

It may now be considered as established that, because there is a considerable spread in the local fields at different points in the crystal, the dipole moments are frozen in random orientations at low temperature, with total absence of long-range order. The situation then resembles what happens in dilute magnetic alloys such as CuAu, in which localized magnetic moments coupled by a sign-varying exchange interaction form a spin-glass state characterized by random orientations of the magnetic moments and zero resultant

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magnetization. Dipole impurities in alkali halide type crystals can therefore be looked upon as electric analogs of spin glasses, and are frequently referred to as dipole glasses. Although the true equilibrium behavior of dipole glass (or of spin glass for that matter) has not been fully elucidated, the observed low-temperature properties can be qualitatively described in terms of long-lived metastable states in which each dipole is aligned along the random local field acting upon it.

The question of ferroelectric order in crystals containing dipole impurities has recently been raised again in connection with the discovery of impurity dipoles in highly polarizable dielectrics ($KTaO_3$, PbTe). It was shown[9] that the attainment of a ferroelectric phase transition in such compounds would be facilitated by spatial dispersion of permittivity, which is usually appreciable in highly-polarizable media. Spatial dispersion, characterized by the spatial polarization correlation length r_c, modifies the effective interaction potential between the dipoles, so that the interaction between the impurities separated by distances $r < r_c$ is mostly ferroelectric, and more long-range than the usual dipole-dipole interaction. It is therefore not of the specific dipole type. The long range character of the interaction ensures that configurational fluctuations in local fields (which destroy the ferroelectric phase transition in weakly-polarizable alkali crystals) are reduced, and long-range order may appear in the system under certain definite conditions.

Does this phenomenon actually occur in practice? This question has been the subject of numerous arguments and discussions that have continued to this day. Nevertheless, it can now be concluded that the situation in highly-polarizable crystals is radically different from that obtained in traditional dipole glass, and there is a wealth of experimental evidence for the impurity-dipole induced ferroelectric phase transition.

Off-center ions are the most characteristic representatives of dipole impurities with cooperative properties. It is clear that, in an ionic crystal, a complex consisting of an off-center impurity and a vacancy (due to the absence of a site atom) will have an electric dipole moment. The direction of such dipoles, i.e., the position of the ion, of which there may be several, is not arbitrary but is determined by crystal symmetry. Thermal or tunnel hopping is possible between different positions. The dipoles are not therefore frozen and, like dipolar molecules such as OH^-, can be oriented by both external and internal electric fields, which is the necessary condition for the appearance of temperature-dependent cooperative effects.

The first off-center ion to be detected[10] was Li^+ in KCl. Off-center ions were subsequently found in many other materials, including classical dielectrics such as alkali halide and alkali earth crystals, as well as other more complicated compounds exhibiting structural phase transitions or lying near the stability threshold. As a rule, the off-center configuration is facilitated by a large difference between ionic radii and polarizabilities of substituent and substituted atoms, which upsets the balance of polarization and repulsive forces at the centrally symmetric point of the unit cell.

Off-center ions give rise to an important change in the properties of crystals. They produce anomalies in specific heat, thermal conduction, and absorption of sound, and they are responsible for singularities in Raman and infrared spectra, as well as for changes in the electric, dielectric, magnetic and other properties. Research in this field has been partially systematized in reviews published in the last few years.[11–15] However, these reviews are largely confined to discussions of the individual properties of off-center ions and their individually independent effect on the host crystal. In contrast, we shall concentrate our attention on cooperative phenomena due to the interaction between impurity dipoles.

The aim of the present review will therefore be to familiarize the reader with modern ideas on the ordering of dilute dipole systems in dielectric crystals. We shall not try to provide an exhaustive account of the entire existing experimental material and the various theoretical models. Instead, we shall concentrate our attention on the way the specific properties of dipole forces lead to particular observable consequences when the particles are randomly distributed.

In Section 2 we shall discuss the dipole glass state in alkali crystals. The reasons for the appearance of ferroelectric order in highly-polarizable crystals containing dipole impurities (off-center ions) will be presented in Section 3, and experimental and theoretical studies of the physical properties of such crystals will be examined in Sections 4 and 5.

2. DIPOLE GLASS IN WEAKLY-POLARIZABLE DIELECTRICS CONTAINING OFF-CENTER IONS

In this section we shall discuss the effect of dipole forces between off-center ions on the low-temperature properties of weakly-polarizable dielectrics, the typical representatives of which are the alkali halide crystals.

(a) Observed properties

We begin by considering typical experimental results in which the characteristic properties of dilute dipole systems are particularly appreciable.

1. Dielectric susceptibility

The first experiments on the dielectric properties of dilute dipole systems were described by Kanzig, Hart and Roberts.[1] This work was substantially extended and generalized by Fiory[3] who investigated the systems KCl:Li, NaBr:F, KCl:OH, and RbCl:OH. These studies were recently continued in Refs. 16 and 17.

All these systems exhibit similar behavior. When impurities are introduced, the permittivity ε rises and assumes a strong dependence on frequency (Fig. 1). The permittivity decreases monotonically with increasing frequency in the range between 10^{-2} and 10^5 Hz, which indicates that there is a considerable spread in the relaxation times. However, provided the temperature is not too low, the frequency dispersion of ε ceases at about 10^{-2} Hz. It may therefore be considered that the temperature anomalies in ε observed at these frequencies (Fig. 2) are not a consequence of the usual relaxation effects.

Figure 2 shows the temperature dependence of the excess permittivity $\Delta\varepsilon = \varepsilon - \varepsilon_0$ of KCl:Li for different concen-

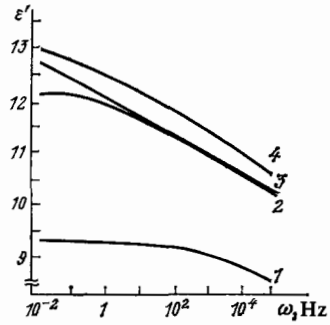

FIG. 1. Real part of permittivity of KCl:Li as a function of the frequency ω ($n = 3\times10^{18}$ cm^{-3}; Ref. 11). T(K) = 1.5 (1), 0.8 (2), 0.25 (3) and 0.4 (4).

trations of the off-center ions (ε_0 is the permittivity of the pure crystal). At high temperatures, $\Delta\varepsilon$ is directly proportional to the concentration of the lithium dipoles, and decreases with temperature as T^{-1} in accordance with the Langevin-Debye law. At low concentrations of the off-center ions, the interactions between them have no observable effect, and the behavior of $\Delta\varepsilon$ is determined by the size of tunnel splitting. When the concentration is raised, a maximum appears on the concentration dependence of $\Delta\varepsilon$, which becomes sharper at higher concentrations. The temperature T_m at which the $\Delta\varepsilon$ maximum appears was determined in Ref. 3 for different dipole systems. It is proportional to the mean energy of the dipole-dipole interaction and satisfies the relation

$$kT_m \approx \frac{nd^{*2}}{\varepsilon_0}, \tag{2.1}$$

where n is the concentration of impurities and d^* is their effective dipole moment which takes into account the Lorentz-field correction. In simple cubic crystals $d^* = (\varepsilon_0 + 2)d/3$, where d is the intrinsic dipole moment, determined by the magnitude of the off-center displacement.

Figure 2 also shows that the excess permittivity observed for $T \gtrsim T_m$ is lower than predicted by the self-consistent mean-field theory in the form of the Clausius-Mossotti equation

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{\varepsilon_0-1}{\varepsilon_0+2} + \frac{4\pi}{3} n\chi_0, \tag{2.2}$$

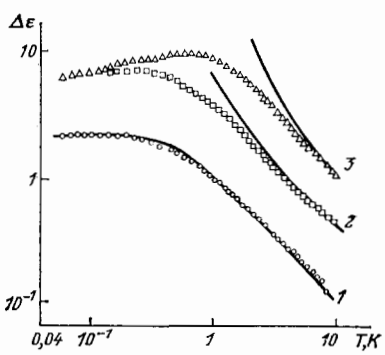

FIG. 2. Temperature dependence of the permittivity excess $\Delta\varepsilon$ of KCl:Li: $n = 10^{18}$ (1), 4.5×10^{18} (2), and 10^{19} (3), all in units of cm^{-3}. The solid curves were calculated from (2.2).

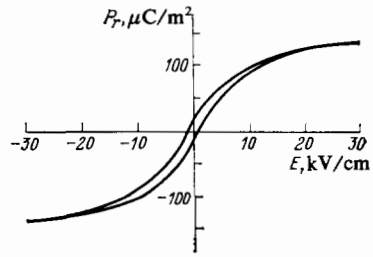

FIG. 3. Hysteresis loop of KCl:Li ($T = 0.06$ K, $n = 3\times10^{18}$ cm^{-3}; Ref. 3).

where $\chi_0 = (2d^2/3\Delta)$ th $(\Delta/2kT)$ is the single-particle polarizability of the noninteracting impurities and χ_0 is the tunneling energy (for Li in KCl, $\Delta/k \simeq 1$ K). Experimental results can be described only if χ_0 in (2.2) is replaced with $\chi_0[1 - (B/T)]$ where $B \approx T_m$. Consequently, the high-temperature behavior of permittivity clearly shows that dipole correlations reduce the polarizability of the system and, hence, prevent the ferroelectric instability ($\varepsilon \to \infty$) that follows from (2.2).

2. Residual polarization

The observed[3] hysteresis loop and residual polarization constitute direct evidence that interacting impurity dipoles can orient one another. The effect was found to be appreciable for $n > 10^{18}$ cm^{-3} and temperatures below 0.3 K. Figure 3 shows a typical hysteresis curve. The loop area decreases at higher temperatures, and hysteresis vanishes altogether for $T > 1$ K. The shape of the hysteresis loop is very different from that observed for ferroelectrics. Moreover, the residual polarization is very small in comparison with ferroelectrics ($P_r \approx 10\%\ nd^*$), and so is the coercive field.

Hysteresis is found to be accompanied by the release of heat, when the field is increased or reduced. At low temperatures, the release of heat by hysteresis impedes the observation of the electrocaloric effect, which was investigated at higher temperatures in Ref. 18.

The residual polarization was also measured by cooling the specimen in an electric field, and then turning off the field. Figure 4 shows that the dependence of the residual polarization on time is logarithmic. The polarization decays vary rapidly at the initial instants of time, but this is subsequently followed by a very slow variation. Figure 5 shows that the dependence of polarization on the concentration n of dipoles is almost quadratic ($Pr \simeq n^2$).

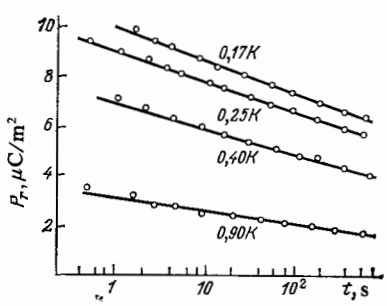

FIG. 4. Residual polarization as a function of time for KCl:Li (Ref. 3).

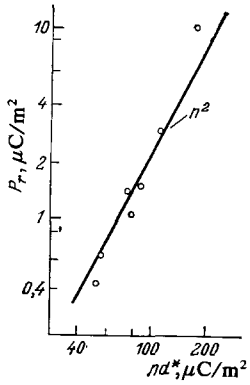

FIG. 5. Concentration dependence of the residual polarization of KCl:Li ($t = 60$ s, $T = 0.2$ K; Ref. 3).

3. Specific heat

The character of the temperature dependence of specific heat changes as the concentration of off-center ions increases.[2] While at low temperatures there is a maximum due to tunneling states, the specific heat increases monotonically with temperature at the higher temperatures that have been attained. No appreciable anomalies have been observed in this behavior near T_m. However, the temperature range of these measurements was limited by the fact that the lattice specific heat, which is approximately proportional to T^3, begins to predominate at higher temperatures. Highly concentrated samples are necessary for the detection of impurity interaction effects because of the high specific heat of tunneling states.

For concentrations above $n \simeq 7 \times 10^{18}$ cm^{-3}, the specific heat varies at low temperatures as[3]

$$C_V \propto n^{-1/2} T^{3/2}. \tag{2.3}$$

Fiory[3] used the analogy with ferromagnets (for which the law $C_V \sim T^{3/2}$ is due to the contribution of spin waves) as a basis for the proposal that polarization waves may occur in dilute dipole systems. However, his detailed studies revealed no indication of the presence of such collective excitations.

4. Absorption of ultrasound

Bayer and Sack[19] have detected cooperative effects in experiments with ultrasound. The effect of off-center ions on the velocity and absorption of sound is due to the interaction between the elastic moments of the off-center ions and lattice deformations produced by the sound wave, which leads to an increase in the elastic compliance of the crystal. At high temperatures, at which the interaction between the impurities has no effect, the change $\delta s/s$ in elastic compliance is determined by the susceptibility of isolated dipoles, and should follow the law $\delta s/s \propto T^{-1}$, by analogy with the temperature dependence of dielectric permittivity. Experiments have shown that, as the temperature is lowered, a departure from this relation is found to occur, and the results can be approximately described by $\delta s/s \propto (T+\theta)^{-1}$. Consequently, the interaction effect reduces not only the polarizability of the electric dipoles coupled to the off-center ions, but also their elastic compliance. The quantity θ is close to T_m, which indicates that dipole-dipole forces play a dominant role in this phenomenon. This conclusion is also confirmed by numerical estimates[19] which have shown that elastic interactions between the off-center ions are indeed of minor importance here.

5. Thermal conductivity

Off-center ions affect thermal conductivity through scattering of phonons by tunneling states. Maximum conductivity should then be observed when the energy of thermal phonons is comparable with the tunnel splitting energy. The dipole-dipole interaction is reflected in the increase in the tunnel energy due to the Stark effect, which is accompanied by an increase in the scattering cross section for the higher frequency and leads to a shift of the thermal resistance maximum toward higher temperatures.[2,3]

Manifestations of the electric dipole-dipole interactions between impurities have also been observed in certain other experiments. In particular, Luti[20] has found a concentration dependence of the electro-optic and elasto-optic coefficients. A concentration dependence of the infrared absorption coefficient has also been reported.[13]

(b) Theoretical Ideas

The experimental data presented above enable us to identify the following basic properties of the cooperative behavior of dipole impurity systems in weakly-polarizable dielectric hosts: (1) interaction effects lower the polarizability of the system and do not produce spontaneous polarization and (2) the presence of residual polarization indicates that the low-temperature behavior of the system is characterized by metastable states with very long relaxation times.

Let us now consider the physics of these phenomena.

The fact that the temperature T_m (2.1) is proportional to the mean dipole-interaction energy is a direct indication that it is precisely this interaction that dominates the situation, although the elastic interaction may also be important in some cases.

It has been shown[21,32] that, when the interaction between electric dipoles in a polarizable medium is considered, it is necessary to take into account the difference between the field acting on a dipole and the macroscopic field. This difference ensures that the dipole-dipole interaction Hamiltonian

$$V_{dd} = \frac{1}{2\varepsilon_0} \sum_{ij} \frac{1}{r_{ij}^3} [\mathbf{d}_i^* \cdot \mathbf{d}_j^* - 3(\mathbf{n}_{ij} \cdot \mathbf{d}_i^*)(\mathbf{n}_{ij} \cdot \mathbf{d}_j^*)] = -\sum_i \mathbf{d}_i^* \cdot \mathbf{E}_i \tag{2.4}$$

contains the effective and not the true dipole moments (we shall return to this point in greater detail in Section 4) where $\mathbf{E}_i$ is the effective local field on the ith dipole due to neighboring impurities and $\mathbf{n} = \mathbf{r}/r$.

Henceforth we shall neglect tunneling effects and will consider classical dipoles. This will not, as a rule, turn out to be a serious limitation because cooperative effects appear only when the mean dipole-dipole interaction energy exceeds the tunnel energy. In fact, it follows[7] from the Hamiltonian (2.4) with classical dipoles that, for $T \gtrsim T_m$, the ef-

fective single-particle polarizability becomes smaller than the polarizability of noninteracting particles $n\chi_0$. To explain this fact, we shall use the virial expansion and represent χ in the form

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

where χ_{12} is the polarizability of a pair of dipoles interacting in accordance with the Hamiltonian (2.4). The integral in (2.5) takes into account the spread in the mutual disposition of the interacting pairs, and leads to an expression of the form

$$\chi = n\chi_0 \left(1 - \frac{B}{T}\right), \tag{2.6}$$

where B depends on the number of possible directions of the dipole in the lattice. For example, for orientations along the [100] direction, we have $B \approx 0.26\, d^{*2} n/k\varepsilon_0$ which is somewhat lower than the experimental value $B \simeq T_m$ in (2.1). Lawless[7] has shown that the agreement with experiment can be substantially improved by excluding from (2.5) the contribution of "frozen-out pairs" whose energy exceeds kT.

It is clear from (2.6) and (2.1) that, when $T \to T_m$, the virial series diverge and the pair approximation fails. Hence the conclusion, derived in the pair approximation, that the polarizability of the system decreases for $T > T_m$ because of the local dipole-dipole interaction (which prevents the ferroelectric phase transition) cannot as yet be regarded as a convincing argument that spontaneous polarization will not appear for $T \ll T_m$ (other approaches, which we will consider below, will be necessary to resolve this problem).

The pair approximation can, however, explain the residual polarization which turns out to be a consequence of the fact that it is difficult to reorient each dipole in a pair because the additional potential barrier due to the neighboring dipole must then be overcome. The closer the dipoles lie together the greater the potential barrier that has to be overcome and, consequently, the longer the relaxation time of the dipole moment of the pair.

Let us now estimate the residual polarization on the assumption that the dipoles can rotate freely.[3] The pair energy minimum then corresponds to two configurations in which the two dipoles are either parallel or antiparallel to the radius vector $\mathbf{r}$ joining them. The mean orientation frequency of the resultant dipole moment of a pair is determined by the potential barrier $W = d^{*2}/\varepsilon_0 r^3$ separating the two minima, and is given by

$$\tilde{\nu} = \nu e^{-W/kT}; \tag{2.7}$$

where ν is the isolated-dipole reorientation frequency.

When the residual polarization frequency is measured at the initial time, all the dipoles are aligned in the external field E_0 and their average dipole moment is $d^* \overline{|\cos\theta|} = d^*/2$ where θ is the angle between $\mathbf{E}_0$ and $\mathbf{r}$, and the bar represents spatial averaging. As soon as the field is turned off, most of the dipoles depolarize rapidly in a time $1/\nu$, but dipoles that have close neighbors take much longer to depolarize, i.e., they take a time $1/\tilde{\nu}$, since the potential barrier must be overcome in the pair depolarization process. Since the separation between the pairs in dipoles is random, the resultant residual polarization is given by

$$P_r = \frac{1}{2} n d^* \int n\, \mathrm{d}r e^{-\tilde{\nu}(W)t}. \tag{2.8}$$

For long enough t, we can substitute $\exp[-\tilde{\nu}(W)t] \approx \theta(W - T\ln(\nu t))$, in (2.8), which substantially simplifies the integral and finally yields

$$\frac{P_r}{nd^*} = \frac{2\pi}{3} \frac{nd^{*2}}{\varepsilon_0 kT \ln(\nu t)}. \tag{2.9}$$

Thus, $P_r \propto n^2$, which is in accord with experiment. However, equation (2.9) predicts the inverse logarithmic dependence of P_r on time, while the experimental data of Fig. 4 are in better agreement with $P_r \propto \mathrm{const} - \ln(\nu t)$. This difference can be explained[23] by the more accurate evaluation of the integral in (2.8), which must be performed for values of t that are not too large. Moreover, allowance for the discrete distribution of dipole orientations reduces the value of the numerical factor in (2.9). For example, when $\mathbf{d} \| [100]$, this factor is 0.4.

The presence of residual polarization clearly shows that, at low temperatures, the system is characterized by metastable states separated by potential barriers. A minimum of the Hamiltonian (2.4) with respect to the possible orientations of each dipole, i.e., a local minimum, is reached[24] in the metastable states. The condition for this minimum yields

$$\mathbf{E}_i = \lambda_i \mathbf{d}_i, \tag{2.10}$$

where λ_i are the Lagrange multipliers corresponding to the conditional extremum of (2.4) with $|\mathbf{d}_i| = \mathrm{const}$. It can be shown that $\lambda_i \geqslant 0$ for all i.

Consequently, in metastable states at $T = 0$, each dipole is parallel to its local field, i.e., the system is characterized by "frozen" configurations of the dipole moments. At finite temperatures (but lower characteristic barrier heights between metastable states), the strength of the local field determines the thermal average of the dipole moment. Hence the basic characteristic of metastable states is the local-field distribution function $f(E) = \delta\, \overline{(E - E_i)}$.

Since the dipole-dipole interaction potential has a variable sign, and the dipoles are randomly distributed in space, the local fields acting on the respective impurities have different directions, so that, at low temperatures, and in the absence of external fields, the dipoles are frozen in random orientations. This low-temperature state of dipoles oriented randomly in internal fields is commonly referred to as a dipole glass, by analogy with spin glass[1)] which has similar properties.[25,26] The same phrase (dipole glass) is also used to describe the system of randomly distributed dipoles.

Let us now consider why such dipole systems do not exhibit spontaneous polarization or long-range ferroelectric order. We shall suppose that, as usual, the crystal is arranged so that there is no depolarizing field, for example, the crystal is located between the plates of a shorted capacitor. The absence of spontaneous polarization is then not obvious because, if we arrange the dipoles so that they all point in the same direction, there will be a nonzero mean local field $\overline{E}_i$ in the system, equal to the Lorentz field, i.e., $\overline{E}_i = (4\pi/3)d^*n$. If configurational fluctuations in local fields are then small,

it is known that the presence of a nonzero mean field ensures at low temperatures that the state with coherently aligned dipoles is energetically the most convenient, and may therefore occur spontaneously. We shall show, however, that configurational fluctuations are important here, so that states with preferred orientation of the dipole moments are not energetically convenient, since they do not satisfy the condition that the local Hamiltonian is a minimum.[27]

We now introduce the unit vector $\mathbf{l}(\mathbf{E})$ which defines the direction of the dipole moment of an impurity in the local field $\mathbf{E}$. It follows from (2.10) that $\mathbf{l}(\mathbf{E}) = \mathbf{E}/E$ as $T \to 0$. If the dipole moments in the system have some preferred orientation at low temperatures, the average

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

will not be zero. The quantity $|\bar{\mathbf{l}}|$ will then be a measure of the relative number of coherently aligned dipoles, and may be looked upon as the order parameter. The answer to the question as to whether this nonzero parameter exists in a dilute dipole system described by the Hamiltonian (2.4) will give us the solution of (2.11) if we first find the dependence of $f(\mathbf{E})$ on $\bar{\mathbf{l}}$.

The function $f(\mathbf{E})$ is readily calculated if we neglect correlations between the orientations of the dipole moments of different particles, and use the random molecular field approximation.[28] For example, if the dipole moments can point along only two possible directions, the function $f(\mathbf{E})$ takes the form

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

where the half-width is $\delta = 5.1\, nd^*/\varepsilon_0$ and the most probable local field is $E_0 \approx 3.5\, nd^*/\varepsilon_0$. Substitution of (2.12) in (2.11) shows that the solution with $\bar{l} \neq 0$ is possible only for $(2E_0/\pi\delta) > 1$, which cannot happen for the above values of E_0 and δ. An analogous result holds for arbitrarily oriented dipole moments.

Consequently, ferroelectric order is completely absent from dipole glasses. This conclusion was first obtained for freely oriented dipoles by a different method.[29] The analysis given above is less rigorous (it employs the random molecular field approximation whose precision has not been verified for dipole systems), but it provides a very clear picture of the role of local-field fluctuations in space, and shows that even small changes in the ratio of E_0 and δ are sufficient to ensure that ferroelectric order will occur. We shall see in the next section that this situation is indeed realized in highly-polarizable crystals.

The random molecular field approximation has been used[28] to describe the thermodynamics of dipole glasses at finite temperatures. It is clear from the foregoing, however, that we have actually been dealing with only quasi-equilibrium properties in metastable states.

In contrast to the $T = 0$ case, not all the dipoles are frozen in local fields at finite temperatures: those whose energy exceeds kT are not. The relative number of frozen dipoles is

$$\mu(T) \equiv \overline{|\langle l \rangle|}, \tag{2.13}$$

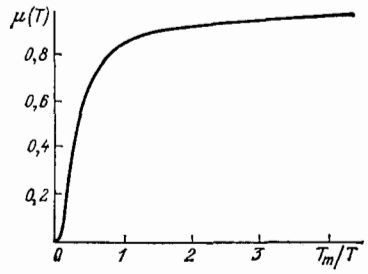

FIG. 6. Temperature dependence of the order parameter of dipole glass.

and this quantity may be looked upon as a measure of long-range order in dipole glass (angle brackets indicate statistical averaging in a given local field). The authors of Ref. 28 assumed right from the outset that $\bar{l} = 0$. The function $f(E)$ found by them is a Lorentzian that is symmetric relative to $E = 0$, and its width is $\delta \propto \mu$. The calculated values of $\mu(T)$ are shown in Fig. 6.

In particular, it is clear that, for $T \simeq T_m$, about 80% of all the dipoles are completely frozen in local fields ($\mu \approx 0.8$). As the temperature increases, $\mu(T)$ rapidly decreases and becomes practically equal to zero at $T \simeq 10 T_m$. The function $\mu(T)$ does not actually become equal to zero at any temperature, since it was assumed that there are configurations in which two dipoles can be located at as short a distance from one another as desired, i.e., at any temperature there are frozen, closely spaced, pairs whose energy exceeds kT. An attempt has also been made[30] to consider a more realistic model by introducing a minimum possible separation between the dipoles. This model removes the nonphysical contribution of closely spaced dipoles (separation less than lattice constant) and predicts that above T_m the permittivity should experience a well-defined cusp at the temperature $T_g \sim \eta^{0.66}$. The behavior of $\mu(T)$ near T_g is then analogous to the behavior of the order parameter intype II phase transitions ($\mu = 0$ when $T > T_g$ and the function $\Delta\varepsilon(T)$ is described by the Langevin-Debye law).

However, careful attempts[16,17,31] to detect experimentally the presence of a cusp $\Delta\varepsilon$, indicating the presence of the phase transition for $T > T_m$, have not been successful. The discrepancy between theory and experiment[30] can probably be explained[30] by the fact that the cusp $\Delta\varepsilon$ is mostly due to closely spaced dipoles whose separation is much smaller than the mean. There are serious doubts as to whether such closely spaced dipoles can be described within the framework of the random molecular field approximation without taking correlation effects into account. Nor is it clear to what extent the description using the local-field distribution function to describe low-lying metastable states at high temperatures can be regarded as valid.

The random molecular field approximation encounters considerble difficulties at lower temperatures as well. For example, the calculated[28] temperature dependence of specific heat has the form $C_V \sim T$ and not $C_V \sim T^{3/2}$ as indicated by experiment. A more serious defect is the prediction that entropy is negative at $T = 0$. This can be traced back to the incorrect behavior of $f(E)$ and $E \to 0$. The random molecular-field approximation gives $f(0) \neq 0$ [this is evident from

(2.12)], which conflicts with the condition for the local minimum of the Hamiltonian.[23]

The local minimum is possible only for $f(0) = 0$. This was first noted for spin glasses by Thouless, Anderson, and Palmer.[32] They showed, by performing the high-temperature expansion of the partition function, that the expression for the local field should contain an additional "Onsager term" that had previously been ignored[28,30] and represents the reaction of the field to the position of the spin moment aligned by it. Analogous considerations apply to the dipole glass as well. The equations obtained by Thouless *et al.*[32] correspond to the Bethe-Peierls cluster approximation (see also Ref. 33), and thus substantially improve the random molecular field approximation. They predict the correct result $f(0) = 0$, and are therefore consistent with the local minimum condition.

Kirkpatrick and Varma[34] have carried out a numerical Monte-Carlo calculation of the local-field distribution function for dipole glass in which they replaced (2.4) with a simpler dependence of the interaction energy on the separation between the dipoles ($V_{dd} \propto \pm r^{-3}$). These calculations have in fact confirmed the presence of the "valley" in the function $f(E)$ near $E \to 0$. If the function $f(E)$ is replaced approximately with $f(E) \propto \sqrt{E}$ as $E \to 0$, it can be shown[34] that the theory then explains the low-temperature behavior of the specific heat, i.e., $C_V \sim T^{3/2}$.

Modern theory thus enables us to explain, at least qualitatively, the basic experimentally observed properties of phenomena occurring in electric-dipole glasses. This particular success of the theory is probably due to the fact that the dipole-dipole interaction potential is well known whereas the form of the interaction potential between magnetic moments in, say, spin glasses is often not accurately known at all.

However, the true equilibrium properties of dipole glass have not been finally elucidated. It is still not clear whether the equilibrium properties will be fully "paraelectric" or whether additional properties, some of which were analyzed for spin glasses in Ref. 35, will be possible in dipole glasses as well.

The behavior of metastable states is not entirely clear either. For example, does the nonequilibrium order parameter $\mu(T)$ appear here as in type II phase transitions, or is there a progressive freezing of increasingly distant dipoles?

3. POSSIBLE APPEARANCE OF FERROELECTRIC LONG-RANGE ORDER IN HIGHLY-POLARIZABLE CRYSTALS

(a) Hamiltonian for the dipole-dipole interaction

Studies of ordering in crystals containing off-center impurities have lead to a new line of research after the discovery[36] in 1974 that Li is an off-center ion when it substitutes for K in the highly-polarizable dielectric $KTaO_3$ whose permittivity is greater by two or three orders of magnitude than the permittivity of alkali halide crystals. The anomalies in the physical properties of $KTaO_3$, which depend on the concentration of off-center ions, are well defined up to $T \sim 100$ K, while in alkali halide crystals such anomalies are appreciable only for $T \lesssim 1$ K. Although this is not unexpected, and can be explained by the large increase in the effective dipole moment d^* [which is evident, for example, from (2.1)], there is the natural question as to whether there is a qualitative difference between the cooperative behavior of off-center ions in highly-polarizable crystals and their behavior in classical dielectrics in which the state of the dipole glass is realized. This difference may occur if the Hamiltonian for the interaction of the dipoles in a highly-polarizable dielectric does not reduce to the usual form given by (2.4).

We must therefore consider in greater detail the basic assumptions underlying the explicit form of the energy of interaction between impurity dipoles in a dielectric crystal. We shall see that highly-polarizable hosts do in fact exhibit singularities[9] due to the substantial spatial dispersion of permittivity in highly-polarizable media.

First, we note that there is an additional interaction between the dipoles in a dielectric because each dipole polarizes the lattice, and this induced polarization acts on neighboring dipoles. The interaction of each dipole with the lattice polarization $P(r)$ is conveyed by the internal field acting on the dipole, which is given by

$$\mathbf{E}_{\text{loc}}(\mathbf{r}) = \sum_q e^{i\mathbf{q}\cdot\mathbf{r}} \left[\frac{4\pi}{3}\gamma\mathbf{P}_q - 4\pi\frac{\mathbf{q}}{q^2}(\mathbf{q}\cdot\mathbf{P}_q)(1-\delta_{q0})\right]; \quad (3.1)$$

where P_q are the polarization Fourier components. The second term in (3.1) corresponds to the macroscopic field averaged over the unit cell. The presence of the Kronecker symbol δ_{q0} ensures that the macroscopic field is zero when the crystal is uniformly polarized. The first term in (3.1) represents the difference between the internal field acting on the dipole and the macroscopic field, and is taken in the form that is valid for wave vectors $q < a^{-1}$ (a is the lattice constant[37] and γ is the local field factor at the location of the dipole).

The validity of the first term in (3.1) implies that the dipole impurities may be regarded as point electric dipoles, i.e., the geometric size of the dipoles must be much smaller than the size of the unit cell. This is the case for the off-center ions. The dependence of γ on the off-center displacement was analyzed in Ref. 38 in the point dipole model.

When polarization inhomogeneous over the sample is produced in highly-polarizable crystals, their optical strength due to the transverse part of the polarization is low. Hence the transverse part of the polarization provides the principal contribution to the local field (3.1), and this is the only part that we shall take into account from now on. Moreover, to be specific, we shall consider slightly anharmonic crystals whose high polarizability is due to the presence of the soft transverse phonon mode.[2)] The Hamiltonian for the system of dipoles interacting with the lattice polarization can be written in the simplified form

$$\mathscr{H} = -\sum_i \mathbf{d}_i\cdot\mathbf{E}_{\text{loc}}(\mathbf{r}_i) + \frac{\alpha_0}{2\omega_0^2}V\sum_{qs}\omega_{qs}^2 P_{qs}P_{-qs}, \quad (3.2)$$

and only the first component of (3.1) can be used for E_{loc}, since for transverse vibrations $(\mathbf{q}\cdot\mathbf{P}_q) = 0$, where ω_0 is the soft-mode frequency, $\omega_{qs}^2 = \omega_0^2 + v^2q^2$, $\alpha_0 = 4\pi/(\varepsilon_0 - \varepsilon_\infty)$ is the reciprocal lattice susceptibility, V is the volume of the crystal, and P_{qs} are the polarization amplitudes connected

with the soft branch that is two-fold degenerate for $q = 0$. (When $q = 0$, the soft mode is three-fold degenerate in a cubic crystal, i.e., $s = 1, 2$ for $q \neq 0$; $s = 1, 2, 3$ for $q = 0$.)

The vibrational kinetic energy is also omitted from (3.2). This is possible in the discussion of dynamic effects if the characteristic dipole reorientation frequencies are $v \ll \omega_0$ (adiabatic approximation).

In the adiabatic approximation, the polarization induced by the dipoles follows instantaneously the instantaneous positions of the dipole moments, and is determined by the condition for the minimum of (3.2) with respect to the amplitudes P_{qs}, i.e., from the condition $\partial\mathscr{H}/\partial P_{qs} = 0$. This gives[3)]

$$P_\alpha(\mathbf{r}_i) = -\frac{\varepsilon_0}{4\pi}\sum_{j\beta} K_{ij}^{\alpha\beta}(\mathbf{r}_{ij})\, d_{j\beta}^*, \tag{3.3}$$

where $d_i^* = \gamma\varepsilon_0 d_i/3$ is the effective dipole moment of the impurity in the highly-polarizable crystal (for $\varepsilon_0 \gg \varepsilon_\infty$). In the long-wave approximation

$$K^{\alpha\beta}(r) = \frac{1}{\varepsilon_0}\left\{-\left(\frac{2}{3}\frac{1}{rr_c^2}e^{-r/r_c} + \frac{4\pi}{3V}\right)\delta_{\alpha\beta}(\delta_{\alpha\beta} - 3n_\alpha n_\beta) \times\left[\frac{1}{r^3} - e^{-r/r_c}\left(\frac{1}{r^3} + \frac{1}{r^2 r_c} + \frac{1}{3rr_c^2}\right)\right]\right\}. \tag{3.4}$$

It is clear from (3.4) that the polarization induced by the dipoles depends on the properties of the medium, which are characterized by the correlation length $r_c v/\omega_0$. When $r_c \lesssim a$, which occurs in weakly-polarizable crystals, we can neglect terms containing the correlation length, and $K(r)$ has the usual form $K(r) \propto r^{-3}$. However, since ω_0 is small in highly-polarizable crystals, terms containing the correlation length [which actually account for the spatial dispersion of the permittivity $\varepsilon_q^{-1} \propto \omega_0^2(1 + r_c^2 q^2)$] become important ($r_c > a$) and modify the functional form of $K(r)$.

The term $\sim 4\pi/3V$ in (3.4) is introduced for convenience [it could have been introduced into (2.4) too]. It does not influence the character of the interaction between the dipoles at finite distances, but allows us to take into account the Lorentz field without explicitly considering the boundary effects that were taken into account in (3.1) by excluding the average macroscopic field, evaluated over the specimen.

Substitution of (3.3) in (3.1) and (3.2) enables us to write down the dipole-dipole interaction energy in the form

$$V_{\mathrm{dd}} = \frac{1}{2}\sum_{ij} K_{ij}^{\alpha\beta} d_{i\alpha}^* d_{j\beta}^* = -\sum_i \mathbf{d}_i^*\mathbf{E}_i. \tag{3.5}$$

In weakly-polarizable crystals, the macroscopic field must also be taken into account in (3.1), and (3.2) must be augmented with the energy of longitudinal modes. Proceeding by analogy with the foregoing, and neglecting spatial dispersion effects, we obtain[9] V_{dd} in the form given by (2.4) with $d^* = d[3 + \gamma(\varepsilon_0 - 1)]/3$, which corresponds to the result in Ref. 21 when $\gamma = 1$. However, it follows from our analysis that, for large values of ε_0, the role of the medium does not reduce merely to the renormalization of the dipole moment.

(b) Suppression of fluctuations and conditions for the appearance of ferroelectric order

The change in the dipole interaction potential in highly-polarizable crystals leads to a number of important consequences. Firstly, for impurity separations $r \lesssim r_c$, fluctuations in the potential that are due to configurational fluctuations of the particles are reduced because the function $K(r)$ varies more slowly than r^{-3} for $r < r_c$ [it becomes $K(r) \propto r^{-1}$ for $r \ll r_c$]. Moreover, it is clear from (3.4) that there is a change in the anisotropic part of the interaction, the average of which is zero (as in weakly-polarizable crystals), and there is a new additional isotropic part which increases the most probable value of the local field acting on each dipole and produced by the neighboring impurities. It is therefore clear that, since the isotropic part of the interaction between the dipoles increases with decreasing separation between them, and the fluctuations in the potential are reduced, the most probable value of the local field exceeds its variance for sufficiently high impurity concentrations. As noted in the last section, this should give rise to long-range ferroelectric order in the system. These qualitative considerations were first put forward in Ref. 9 and were subsequently confirmed more rigorously in Ref. 27 by a numerical evaluation of the local field distribution $f(E)$ at $T = 0$. This was carried out by the random molecular field method, followed by the evaluation of the parameter $\bar{l} = \bar{d}/d$, based on the self-consistent equation (2.11).

The results of these calculations in the case of two possible dipole orientations are reproduced in Fig. 7 and show that the "nucleation" of ferroelectric order, i.e., the appearance of a solution with nonzero mean dipole moment, occurs for relatively low values of the parameter nr_c^3, where the critical concentration above which $\bar{l} \neq 0$ corresponds to the condition $n_{\mathrm{cr}} r_c^3 \approx 0.5 \cdot 10^{-2}$. For six possible orientations of the dipoles, the critical concentration is somewhat higher[4)]: $n_{\mathrm{cr}} r_c^3 \approx 10^{-2}$.

We thus see that the change in the character of the forces acting between the off-center ions in highly-polarizable crystals should lead to essentially different cooperative phenomena in such impurity systems as compared with those observed in alkali crystals.

We now turn to the experimental situation.

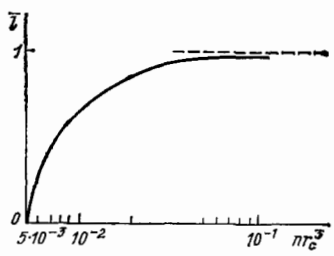

FIG. 7. Long-range ferroelectric order parameter as a function of nr_c^3 (Ref. 27).

4. EXPERIMENTAL STUDIES OF HIGHLY-POLARIZABLE CRYSTALS CONTAINING OFF-CENTER IONS

(a) Off-center ions in highly-polarizable lattices

Experimental studies of off-center ions in highly-polarizable dielectrics were begun much later than the corresponding studies of alkali halide crystals, and are still not sufficiently systematic. There are still relatively few systems for which the off-center nature of impurities has been reliably established.

1. Li^+ in $KTaO_3$

The off-center character of Li in potassium tantalate was first discovered in Raman experiments[36] which demonstrated the presence of a first-order peak. This peak was ascribed to a resonance impurity mode induced by the off-center Li. Subsequent precision measurements[40] on Raman spectra showed that, although the conclusion[36,41] that Li was off-center was correct, the peak observed in the Raman spectrum was not related to a resonance mode but was due to quasi-static fields of lithium dipoles. These fields modify selection rules and enable us to observe first-order scattering by the lattice modes. Figure 8 shows that the intensity of first-order scattering by acoustic and optical vibration branches increases with increasing Li concentration. However, the first-order peaks are appreciable even for nominally pure specimens, which is probably due to the presence of extraneous impurities.

The off-center character of Li ions is also indicated by dielectric, NMR and ESR studies. Measurements[42,43] of the frequency dependence of the permittivity of $KTaO_3$ have shown that the presence of Li leads to a low-frequency dispersion of ε. This suggests that the reorientation of the impurities between different off-center positions has a relaxation character. The reorientation frequency satisfies the Arrhenius law

$$\nu = \nu_0 e^{-U/T} \tag{4.1}$$

with $\nu_0 \approx 1.6 \cdot 10^{-3}\ s^{-1}$ and $U \approx 1000$ K. This high barrier ensures that, for $T \lesssim 30$ K, the characteristic reorientation time exceeds tens of seconds, which is much longer than the experimentally realized times of observation. Hence the low-temperature dynamics of Li appears to be frozen-out in such

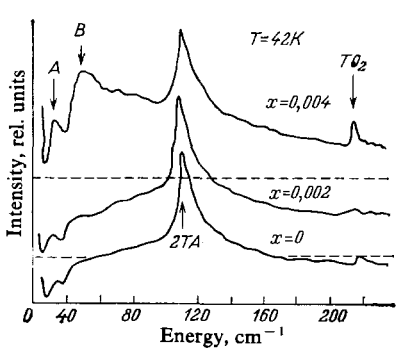

FIG. 8. Raman spectra of $K_{1-x}Li_xTaO_3$ (Ref. 40). Peaks A and B are due to first-order scattering by acoustic and soft optical vibrations, respectively.

experiments. However, this freezing-out is of single-particle character, i.e., it occurs for Li concentrations that are as low as desired, and must not be confused with the cooperative effects considered in the last section. Because of the single-particle character of the thermal freezing of the off-center ions at low temperatures, the residual polarization must be a linear function of n, and this has been confirmed experimentally. Measurements of the residual polarization for low Li concentrations have been used[43] to show that the direction of the off-center displacement of Li is [100].

This was subsequently confirmed by an analysis[44,45] of the quadrupole splitting of the 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 intracrystalline electric field. Since in the centrally-symmetric position of the unit cell in the cubic crystal the electric-field gradient is zero (this is a consequence of the Laplace equation), the appearance of quadrupole splitting unambiguously indicates the off-center character of the ion. The direction of the off-center displacement, which is the axial line of the electric-field gradient, is determined by the dependence of the number and position of the quadrupole satellites on the direction of the magnetic field. Measurements of the quadrupole splitting can also be used to estimate the absolute off-center displacement x_0. The necessary relationship between ν_Q and x_0 was obtained from the point-ion model, and by taking into account polarization and repulsion forces. This gives $x_0 \approx 1.2$ Å.

The thermal reorientations of Li should lead to the averaging of the spectrum and to the vanishing of the quadrupole satellites for $\nu > \nu_Q$, which occurs for $T > 50$ K. In this high-temperature region, the modulation of the intracrystalline field gradient by the motion of the ion produces nuclear spin-lattice relaxation. The reorientation frequency determined by spin-relaxation experiments[40] is in agreement with dielectric measurement data.

Since the reorientation of impurities influences the elastic properties of crystals, measurements have been undertaken[47,48] of the velocity of sound in $KTaO_3$:Li. The observed softening of the elastic moduli $c_{11}-c_{12}$ and the virtual constancy of c_{44} support the displacement of the Li along the [100] direction (the off-center ion then interacts only with the E_g deformation).

The reorientational Li dynamics has also been investigated by electron spin resonance.[49] The magnetic probes were axial Fe^{3+} centers. Because of the random spatial disposition of the Li ions relative to the paramagnetic probes, the ESR line was broadened by the internal electric and elastic fields due to the off-center ions. At low temperatures, the broadening is quasi-static and inhomogeneous, whereas for $T > 90$ K, for which the values of ν are sufficiently high, the lines exhibit dynamic narrowing analogous to the averaging of quadrupole structure in NMR. The observed temperature dependence of the broadening shown in Fig. 9 has been used[49] to determine ν_0 and U, and the results agree with dielectric measurements.

Dielectric[50] and ESR[49] data have also been used to deduce the effective dipole moment d^* of Li, which turned out

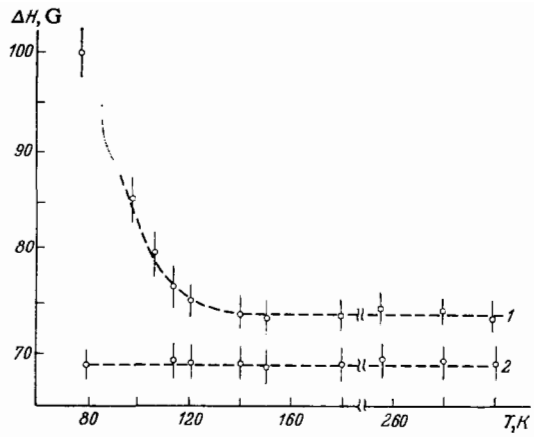

FIG. 9. Temperature dependence of the ESR linewidth of the axial center Fe^{3+} in $K_{0.99}Li_{0.01}$ (1) and in pure TaO_3 (2) (Ref. 49).

to be greater by a factor of 20–30 than the intrinsic dipole moment $d = ex_0$, and is in agreement with the result $d^* = \gamma\varepsilon_0 d/3$ obtained in the last section ($|\gamma| \approx 0.1$ in the point-dipole model).

Experimental data are thus seen to confirm reliably the off-center character of Li in $KTaO_3$.

It is sometimes suggested in the literature[51,52] that the off-center ions in $KTaO_3$ are not only Li but also Na and Nb. However, recent NMR experiments[53,54] have shown that if Na is in fact the off-center ion, then its off-center displacement is very small ($x_0 < 0.1$ Å according to Ref. 53, which is in agreement with the earlier estimate[55]). Calculations[46] of the adiabatic potential also indicate that Na does not exhibit off-center features. Recent studies suggest that the Nb ions occupy centrally-symmetric positions, although it is still not entirely clear which model of the local Nb potential is more satisfactory.[57,58]

2. Ge^{2+} in PbTe

The experimental evidence for the off-center position of Ge^{2+} in PbTe is much less direct than in the case of Li in $KTaO_3$. Logachev and Moĭzhes[59] were the first to deduce the off-center position from an analysis of experimental thermal conductivity data. This conclusion is also supported by the difference between the ionic radii of Ge (0.73 Å) and Pb (1.2 Å). The off-center hypothesis was later put forward in Ref. 60 and was confirmed experimentally[61,62] by measurements of the specific heat of PbTe:Ge. The high-temperature specific heat anomalies shown in Fig. 10 are due to the concentration-dependent effects discussed in section (c) below. On the other hand, the low-temperature peak at $T \approx 17$ K is independent of the concentration of Ge and is due to the contribution of tunneling states (by analogy with the situation in KCl:Li). The tunnel energy $\Delta \approx 17$ K is, however, unusually high. Thus, in contrast to Li in $KTaO_3$, it is found that Ge in PbTe is an example of an off-center ion, the reorientation of which is of dynamic rather than relaxation character. We shall see in section (c) that the assumption of off-center Ge can explain many of the properties of the ferroelectric transition in $Pb_{1-x}Ge_xTe$.

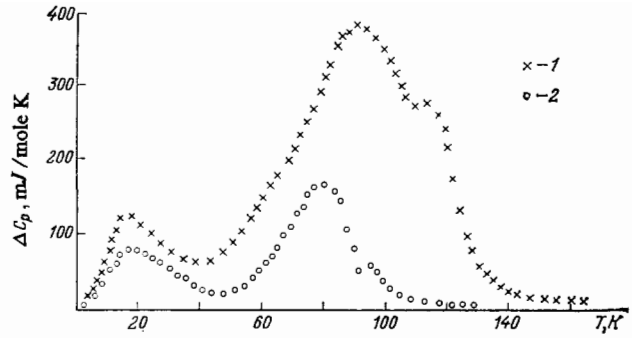

FIG. 10. Temperature dependence of the specific heat of $Pb_{1-x}Ge_xTe$ for $x = 0.038$ and 0.029 (Ref. 62).

3. Origin of the off-center position

It is quite clear that a reduction in repulsive forces or an increase in the polarization of an impurity ion, as compared with the lattices ion it replaces, will favor the off-center effect. It follows that impurities whose radii are smaller and whose polarizations are greater than those of the lattice ions they replace will also be off-central. The use of experimental data on ion polarizability and repulsion parameters has resulted in calculations of the adiabatic potential for certain impurities in alkali halide crystals[63–65] and in $KTaO_3$:Li (Ref. 46), and it has been shown theoretically that the off-center position should indeed occur.

From the point of view of electronic structure, the existence of closely-spaced levels of opposite parity should be favorable for the off-center effect. In that case, the displacement of an impurity from a lattice site[66] is facilitated by the pseudo-Jahn-Teller effect[67] which is equivalent to polarization forces.

Höck and Thomas[68] were the first to draw attention to the fact that in soft, highly-polarizable, lattices or in crystals with structural phase transitions in which there is a strong temperature dependence of lattice vibration frequencies, the off-center effect (i.e., multivalley character of the adiabatic potential) can occur below a well-defined finite temperature T_{loc}. This is sometimes referred to as the "local phase transition" or "local freeze-out", since it follows from the crude description based on the mean field approximation. In reality, there is no freeze-out, but a slow reorientation of the ion between different minima occurs[51,52] below T_{loc}. The characteristic feature of the phenomenon is the temperature dependence of the height of the activation barrier in (4.1) $[U = U(T)]$.

The temperature dependence of the barrier height was recently discovered[69,70] by the ESR method in the paramagnetic centers CrO_3, AsO_4 in KH_2PO_4, $KH_2A_sO_4$, $NH_4H_2A_sO_4$.

It has been shown[71] by considering the off-center displacement as the result of the pseudo-Jahn-Teller effect that a temperature-dependent barrier between the off-center positions may occur in ordinary weakly-polarizable lattices.

(b) Experimental verification of the change in dipole fields in highly-polarizable crystals

We showed in Section 3 that the local electric fields produced by dipolar impurities in highly-polarizable crys-

tals will ensure that for dipole distances shorter than the correlation length r_c, the local field[5)] will decrease more slowly than in ordinary crystals. We can therefore speak of long-range interactions, extending to distances of the order of r_c.

A method for studying dipolar fields through measurements of broadening of ESR lines due to paramagnetic "probes" introduced into the crystal has recently been proposed.[72,49]

Let us consider the frequent situation in which the resonance-frequency shift is a linear function of the local field acting on the paramagnetic center. For a fixed configuration of the dipolar impurities, this shift is given by

$$\Delta\omega = \sum_{j\alpha\beta} p_\alpha^* K_{ij}^{\alpha\beta} d_{j\beta}^*, \tag{4.2}$$

where p^* is the effective dipole moment of the paramagnetic center. Randomness in the disposition of the dipolar impurities then leads to a spread of the resonance frequencies and, hence, to a broadening of the line. The line shape then repeats the dipole field distribution function. For the usual law $K(r) \sim r^{-3}$, the shape of the ESR line is Lorentzian (see, for example, Ref. 73), and its width is a linear function of the concentration of dipoles ($\delta \sim n$).

Enhancement of the long-range interaction in highly-polarizable crystals ensures that when the mean separation between the dipoles is less than r_c, i.e., when $nr_c^3 > 1$, each of the many particles present within a sphere of radius r_c provides roughly the same contribution to the shift of the resonance frequency. The central limit theorem of probability theory is then valid and predicts that the line shape should be a Gaussian of width $\delta \sim n^{1/2}$. Hence for arbitrary values of the parameter nr_c^3, the line shape should be intermediate between a Gaussian and a Lorentzian, and the concentration dependence of its width should be slower than the linear dependence.

These are precisely the ESR line-broadening properties observed in $KTaO_3$:Li for the axial Fe^{3+} center which exhibits a linear electric-field effect and can linearly interact with

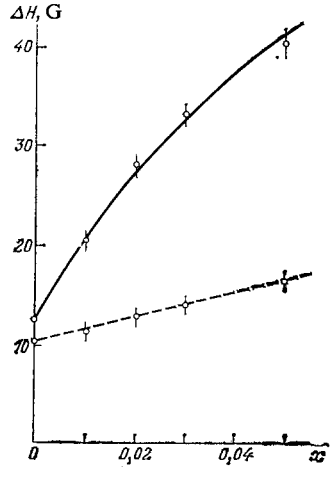

FIG. 11. ESR linewidth of the axial center Fe^{+3} as a function of the concentration of Li in $K_{1-x}Li_xTaO_3$ (Ref. 49).

the internal electric fields produced by off-center Li^+ ions. Figure 11 shows the concentration dependence of the linewidth, and it is clear that the theory[74] [based on the statistical method of calculating the line shift with allowance for (4.2) and (3.7)] is in good agreement with experiment.

The experimentally observed nonlinear concentration dependence of the linewidth, which is due to the electric dipole mechanism of broadening by off-center ions in a highly-polarizable crystal, and the observed deviation of the line shape from the Lorentzian, appear to reflect the longer-range (within the length r_c) character of dipole forces in highly-polarizable crystals.

It is important to note that this type of enhancement of the range of action of fields produced by defects is a general property of soft lattices near the stability threshold (see, for example, Ref. 75). In crystals exhibiting an actual structural phase transition (in contrast to the situation obtaining in $KTaO_3$), the correlation length is found to rise rapidly near the phase transition temperature, so that even for low uncontrollable defect concentrations, the parameter nr_c^3 can undergo a considerable increase, leading to the Gaussian shape of the ESR line.[76] This appears to happen[77] in $SrTiO_3$.

It has been shown[78] that the Gaussian character of the ESR line near T_c should appear not only when the resonance-line shift is a linear function of the local order parameter, but also when the dependence is quadratic.

(c) Cooperative effects

The properties of highly-polarizable crystals that depend on the concentration of off-center ions are very different from those of alkali halide crystals described in Section 2. We begin with a more detailed discussion of the situation in $KTaO_3$:Li, and consider the nature of the ordered state that has been under discussion for a considerable time.

Pure potassium tantalate is a virtual ferroelectric and exhibits paraelectric properties at any temperature. Its dielectric permittivity increases as the temperature is reduced, reaching $\varepsilon_0 = 5 \times 10^3$ at $T = 4$ K. When Li is introduced, the permittivity is found to have a sharp peak which shifts toward higher temperatures as the concentration of off-center ions increases.

It appears that the first observations of dielectric anomalies in $K_{1-x}Li_xTaO_3$ were made by Davis but remained unpublished (the literature frequently quotes another paper by Davis[79] which, however, reports only the data for $KTaO_3$:Na). Yacoby and Just[36] have pointed out that the dielectric anomalies which appear when Li is introduced (they have been ascribed by some authors to a ferroelectric phase transition) cannot be explained by a simple change in the size of the unit cell due to the presence of the impurity ions, as is often the case in virtual ferroelectrics. The addition of Li reduces the size of the unit cell,[36] but hydrostatic experiments[80] have shown that the permittivity decreases with decreasing size of the unit cell, and the crystal does not become ferroelectric. The anomalies in the properties of $KTaO_3$:Li can be naturally related to the off-center nature of Li.

In $K_{1-x}Li_xTaO_3$, as in alkali halide crystals containing

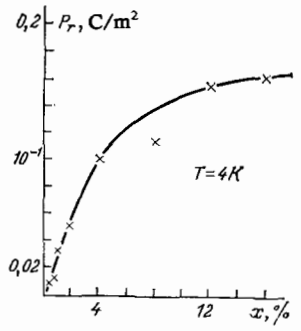

FIG. 12. Residual polarization at $T = 4$ K as a function of Li concentration in $K_{1-x}Li_xTaO_3$ (Ref. 43).

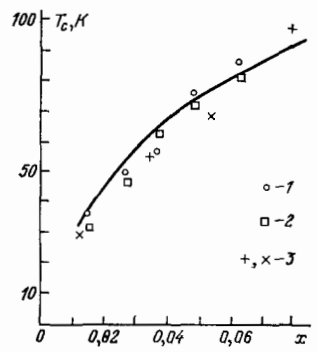

FIG. 14. Ferroelectric phase transition temperature as a function of Li concentration in $K_{1-x}Li_xTaO_3$ (Ref. 45), obtained by different methods: 1—birefringence, 2—dielectric measurements, 3—Raman scattering. Solid curve was calculated from $T_c = 300x^{1/2}$ K.

off-center ions, spontaneous polarization has not been determined by direct measurement, but residual polarization has been observed,[43] and was found to increase with increasing x (see Fig. 12). This type of dependence is very different from the relation $P_r \sim x^2$ ($x = na^3$) found for alkali halide crystals. The temperature dependence $P_r(T)$ (Fig. 13) is also different: it rises rapidly[45] for $T < T_c$ (T_c is the temperature corresponding to the permittivity maximum, near which all the properties of the crystal that depend on the concentration of Li are found to exhibit anomalies). The concentration dependence of T_c is slower than the linear dependence (Fig. 14), in contrast to the linear concentration dependence in (2.1).

The frequency dispersion of permittivity exhibits unusual properties as well. It has been shown[45,81,50] that two different relaxation mechanisms are responsible for the dispersion of permittivity for $x > 0.04$. The high-frequency relaxation mechanism has an activation energy of about 1000 K and is related to the independent motion of the individual off-center ions (well away from T_c). The activation energy of the low-frequency relaxation mechanism, the nature of which is still not entirely clear, is higher by a factor of about 2.5. The characteristic frequencies of both relaxation processes fall critically as $T \to T_c$.

Although the above experimental data show that the behavior of off-center ions in potassium tantalate differs from the situation in alkali halide crystals, they were not sufficient to resolve the question as to whether the low-temperature state is ferroelectric or whether here again a dipole glass state is produced (at least within a restricted range of Li concentrations). The latter point of view has been supported in the literature,[43,45,82,83] and has been claimed[45] to be

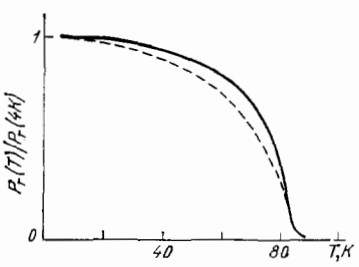

FIG. 13. Temperature dependence of residual polarization of $K_{1-x}Li_xTaO_3$ for $x = 0.063$ (Ref. 45). Broken curve was calculated from (5.12).

further supported by experiments[44] in which no evidence was found for anomalies in the spin-lattice relaxation rate near T_c.

Different groups have performed additional experiments[40,84–86] which have elucidated the nature of the phenomenon and have led to the conclusion that $KTaO_3$:Li exhibits a ferroelectric phase transition.

Thus, studies of birefringence have shown that relatively large polar regions appear below T_c. They take the form of domains[40] with linear dimension of about 5000 Å and lie along the [100] direction, with regularly distributed[86] domain walls. It is clear that this picture is not consistent with traditional ideas on the dipole glass state, in which short-range order extends to only a few nearest coordination spheres.

A still more convincing argument in favor of the ferroelectric phase transition in $KTaO_3$:Li at $T = T_c$ is provided by the observed[40,85] splitting of the Raman peak corresponding to the soft-mode frequency (peak B in Fig. 8), which clearly indicates 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. 15, from which it is also clear that the soft-mode frequency has a finite value at $T = T_c$, which is characteristic for phase transitions of the order-disorder type.

Also inconsistent with the concept of the dipole state is

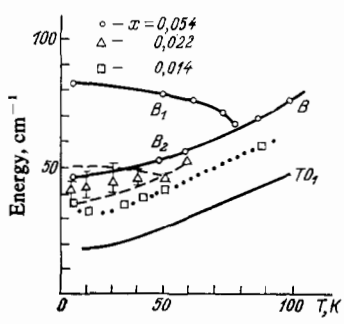

FIG. 15. Temperature dependence of the soft-mode frequency of $K_{1-x}Li_xTaO_3$ and of pure $KTaO_3$ (curve TO_1; Ref. 40). Vertical bars indicate the magnitude of unresolved splitting for $x = 0.022$.

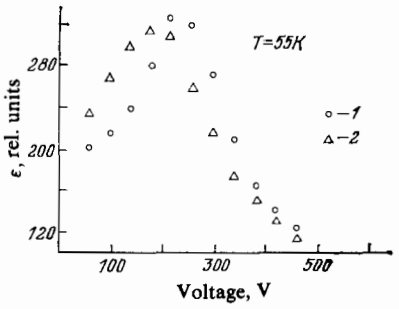

FIG. 16. Permittivity of $K_{1-x}Li_xTaO_3$ for $x = 0.035$ as a function of applied voltage[87]: 1—increasing voltage, 2—decreasing voltage.

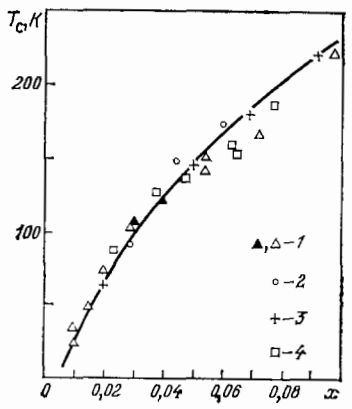

FIG. 17. Ferroelectric phase transition temperature as a function of Ge concentration in $Pb_{1-x}Ge_xTe$ (Ref. 90), obtained by different methods: 1—electrical conductivity, 2—permittivity, 3—x-ray scattering, 4—ultrasound absorption.

the discovery[87] of the anomalous rise in the nonlinear dielectric response in a certain temperature range when the external electric field is increased, which can be seen in Fig. 16 (the anomalies are smoothed out in the electric field in the case of the dipole glass). At the same time, it has been shown[87] that the character of the dielectric anomalies is in complete agreement with the assumption of a type I ferroelectric phase transition, whereas above T_c there is a change in the sign of the dielectric nonlinearity factor b_1.[6)] The latter assumption is also supported by earlier experiments.[84] Acoustic anomalies[88,48] can also be regarded as evidence for ferroelectric ordering.

Summarizing our brief review of the experimental situation in relation to $KTaO_3$, we may conclude that, even without a detailed theoretical analysis of singularities in the physical properties of highly-polarizable crystals containing off-center ions, which will be partly carried out in the next section, there is an essential difference between the character of cooperative behavior in highly-polarizable crystals and those that are difficult to polarize. This suggests that the ferroelectric phase transition does occur in highly-polarizable crystals.

A ferroelectric phase transition induced by off-center ions is also observed in $Pb_{1-x}Ge_xTe$. Pure PbTe is similar to $KTaO_3$ in that it is a virtual ferroelectric and has an anomalously high permittivity. When Ge is introduced, a transition is observed to a phase with rhombohedral symmetry in which spontaneous polarization appears along the [111] direction. This phase transition was first observed[89] by the x ray scattering method prior to the discovery of the off-center nature of the Ge. The singularities in the physical properties of PbTe:Ge near the ferroelectric phase transition point were subsequently examined by different methods, including measurements of electrical resistance, absorption of sound,[90] permittivity,[91] and specific heat.[61,62] Figure 17 shows the concentration dependence of the phase transition temperature deduced from these data. Figure 18 shows the measured[89] temperature dependence of the rhombohedral distortion angle of the lattice.

The fact that off-center Ge is actually responsible for the phase transition in $Pb_{1-x}Ge_xTe$ is indicated by the series of unusual properties of this mixed crystal as compared with, for example, the structurally similar $Pb_{1-x}Sn_xTe$ in which the phase transition is due to the electron-phonon interaction.[90] Thus, the phase transition temperature rises very rapidly in $Pb_{1-x}Sn_xTe$ with increasing Ge concentration, reaching $T_c = 200$ K at $x = 0.1$. Moreover, the temperature dependence of the permittivity is very different from the Curie-Weiss law (Fig. 19), and singularities in electrical resistance[90] cannot be explained without introducing off-center Ge. Recent experiments on the effect of hydrostatic pressure,[92] in which the phase transition temperature was found to decrease strongly, and the transition itself disappeared altogether above about 4 kbar, can also be readily explained in terms of the usual increase in tunneling frequency of off-center ions under increased pressure, due to the smaller off-center displacement.

5. ANOMALIES IN CRYSTAL PROPERTIES DUE TO THE FERROELECTRIC PHASE TRANSITION INDUCED BY OFF-CENTER IONS (THEORY)

We must now consider the basic physical properties of crystals in which off-center ions induce a ferroelectric phase transition.

(a) Range of validity of the self-consistent field approximation

The validity of the mean-field approximation has been investigated[27] by evaluating the Ginzburg-Levanyuk criterion in the form of the ratio of the first fluctuation correction ΔC to the specific field to the jump in specific heat C_0 given by the mean-field approximation. The condition for small fluctuations is

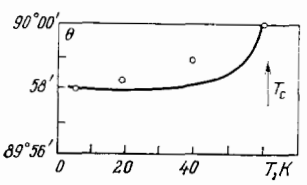

FIG. 18. Temperature dependence of rhombohedral distortion angle of the lattice below T_c in $Pb_{0.98}Ge_{0.02}Te$ (Ref. 89). Solid curve—calculated in Ref. 60.

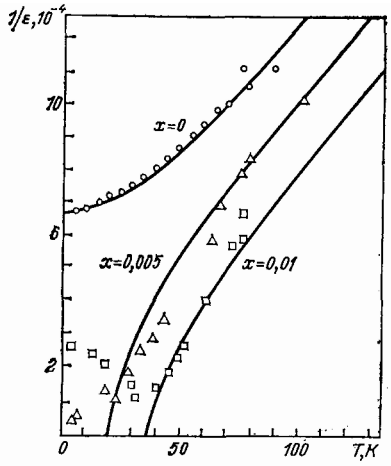

FIG. 19. Temperature dependence of the reciprocal permittivity of $Pb_{1-x}Ge_xTe$. Solid curves—calculated in Ref. 60.

$$\frac{\Delta C}{C_0}=\frac{\mathrm{Gi}}{\sqrt{\tau}}\ll 1,\quad \tau=1-\frac{T_c}{T}\frac{\varepsilon_0(T)}{\varepsilon_0(T_c)},\tag{5.1}$$

where T_c is the ferroelectric transition point in the mean-field approximation,

$$kT_c=\frac{4\pi}{3}\frac{d^{*2}n}{\varepsilon_0},\tag{5.2}$$

and the Ginzburg-Levanyuk number Gi for, say, freely orientable dipoles is[27]

$$\mathrm{Gi}=\frac{1}{20\pi\sqrt{m}\,nr_c^3},\tag{5.3}$$

where $m=(1+\varepsilon_0T\partial\varepsilon_0^{-1}/\partial T)$.

The fact that the number Gi is small indicates that, for $\sqrt{|\tau|}\gg\mathrm{Gi}$, the description in terms of the self-consistent field is a valid approximation[93] although the Ginzburg-Levanyuk criterion is not a universal qualitative criterion, so that, for example, the numerical coefficient in (5.3) may turn out to be different in the analogous calculation of fluctuational corrections to the susceptibility. However, comparison with numerical calculations for spatially ordered systems with nearest-neighbor interactions shows that for $\mathrm{Gi}\leqslant 1/6$ ($z=1/\mathrm{Gi}$ is the effective number of interacting nearest neighbors), the mean-field approximation introduces an error of not more than 30% in the calculated phase transition temperature. It may therefore be assumed that, for $\mathrm{Gi}\lesssim 1/6$, i.e., according to (5.3) for $nr_c^3\gtrsim 10^{-1}$, the mean-field approximation is valid for our system with approximately the same precision. This conclusion agrees with the results of the analysis given in Section 3 for the low-temperature region. Thus, it is clear from Fig. 7 that the mean-field approximation, which corresponds to $\bar{l}\approx 1$ for $T=0$ (parallel orientation of all dipole moments), is approximately valid for $nr_c^3\gtrsim 10^{-1}$.

A similar estimate of the range of validity of the mean-field theory has been deduced[94] from an analysis of the high-temperature behavior of the susceptibility. This involved a calculation of the effective polarizability of the dipoles by means of a virial expansion analogous to (2.5). To within the second virial coefficient, we have

$$\chi=n\chi_0\left(1-\frac{B(d^{*2}/\varepsilon_0kTr_c^3)}{T}+\frac{4\pi}{9}\frac{nd^{*2}}{\varepsilon_0kT}\right).\tag{5.4}$$

The function $B(d^{*2}/kTr_c^3\varepsilon_0)$ has been evaluated numerically[94] and has the following asymptotic representations:

$$B\left(\frac{d^{*2}}{\varepsilon_0kTr_c^3}\right)=\frac{nd^{*2}}{k\varepsilon_0}\times\begin{cases}-\dfrac{8\pi}{9}, & \dfrac{d^{*2}}{\varepsilon_0kTr_c^3}\ll 1, \quad (5.5a)\\[2ex] 0.26, & \dfrac{d^{*2}}{\varepsilon_0kTr_c^3}\gg 1. \quad (5.5b)\end{cases}$$

Expression (5.5b) corresponds to the limit of weakly-polarizable crystals with the usual dipole interaction (2.4). However, the opposite limit (5.5a) occurs for higher values of r_c and corresponds to the self-consistent mean-field approximation.

We now draw attention to the fact that the polarizability (5.4) is related to the response of the system of dipoles to the mean macroscopic field and not the local field as assumed in the derivation of (2.4). With this definition [which ensures that, in contrast to (2.4), expression (5.4) acquires the additional last term], the relation between χ and $\Delta\varepsilon$ has the usual form $\Delta\varepsilon=4\pi\chi$, and there is no need to invoke the Clausius-Mossotti equation.

Expression (5.4) can be used to estimate the characteristic temperature T_c^* below which the virial series diverge. This temperature is determined from the condition that the sum of the second and third terms in parenthesis in (5.4) is equal to unity. The values of this sum are plotted in Fig. 20. It is clear that appreciable deviations of T_c^* from the mean-field theory in which $T_c^*=T_c$ begin only for $nr_c^3\lesssim 10^{-1}$.[7)] We also note that, since outside the region of validity of the mean-field theory, the temperature T_c^* is equal to the ferroelectric transition temperature, it is hoped that the qualitative correspondence between T_c^* and the true transition temperature will remain even outside the range of validity of the mean-field approximation, at least for small differences between T_c^* and T_c. In that case, the relationship between T_c^* and nr_c^* shown in Fig. 20 should reflect qualitatively the effect of spatial particle fluctuations on the ferroelectric transition temperature. This is also indicated by the calculations, shown in the same figure, of the phase transition temperature in the random molecular field approximation.

When T_c^{RMF} was calculated, allowance was made for the fact that, since near the phase transition point the mean dipole moment is vanishingly small, the approximation used[27] to estimate n_{cr} is also valid for the evaluation of $f(E)$. The only difference lies in the way the thermal average of the

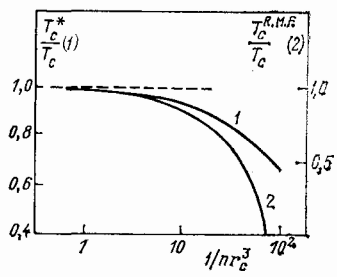

FIG. 20. T_c^* and the ferroelectric phase transition temperature T_c^{RMF} in the random molecular field approximation as functions of the parameter nr_c^3 [T_c is the phase transition temperature in the mean-field approximation, defined by (5.2)].

mean dipole moment is written (it must take into account the fact that the temperature is finite).

(b) Phase transition temperature and stochastic susceptibility

Henceforth, we shall assume condition (5.1) for the validity of the mean-field theory (and of the random-phase approximation for the fluctuations). The phase transition temperature will then be defined by (5.2), but it will be necessary to allow for the fact that ε_0 is usually a function of temperature in highly-polarizable crystals, so that the explicit dependence of T_c on the parameters can be obtained only for a known relationship between ε_0 and T. For example, if we approximate $\varepsilon_0(T)$ by the Curie-Weiss law $\varepsilon_0(T) = C/(T-T_0)$, we obtain from (5.2).

$$T_c = \frac{1}{2}\left(T_0 + \sqrt{T_0^2 + \frac{16\pi\gamma^2 d^2 Cn}{27k}}\right). \tag{5.6}$$

It is clear from (5.6) that the absence of reorientating dipole impurities increases the phase transition temperature of the pure crystal. This fact was first considered[8)] (within the framework of another model) by Halperin and Varma,[95] but only terms linear in n were included in that analysis. However, it follows from (5.6) that if there is no phase transition in the pure crystal, i.e., $T_0 \simeq 0$, the temperature T_c is not a linear function of the concentration, but is proportional to $n^{1/2}$.

Formula (5.2) can readily be generalized to the case where off-center ion tunneling becomes important.[55,60] The temperature T_c is then determined from

$$\frac{4\pi}{3}\frac{d^{*2}}{\varepsilon_0} n \frac{1}{\Delta}\tanh\frac{\Delta}{kT_c} = 1. \tag{5.7}$$

Since tunneling effects impede the onset of the ferroelectric phase transition, they constitute an additional reason for the appearance of the critical concentration. To find this concentration, we set $T_c = 0$ in (5.7) and obtain

$$n_{cr} = \left(\frac{3\Delta\cdot\varepsilon_0}{4\pi d^{*2}}\right)_{T=0}. \tag{5.8}$$

When $\Delta/k > 1$ K, the critical concentration due to tunneling will usually exceed the values due to the effect of spatial fluctuations, which were discussed in Section 3.

In the mean-field approximation, the static permittivity (for $\Delta \to 0$, $T \to T_c$) has the form

$$\varepsilon^{-1}(T) = \varepsilon_0^{-1}(T) - \frac{T_c}{T}\varepsilon_0^{-1}(T_c), \tag{5.9}$$

which, in general, differs from the Curie-Weiss law because ε_0 depends on temperature.

A somewhat more complicated form of $\varepsilon(T)$, which takes tunneling effects into account, has been given by Katayama and Murase.[60]

(c) Anharmonic-lattice effects. Spontaneous polarization

The Hamiltonian (3.2) does not include the terms that are nonlinear in the polarization, i.e.,

$$\mathscr{H}_{anh} = \int d\mathbf{r}\left(\frac{b_1}{4}\sum_\alpha P_\alpha^4 + \frac{b_2}{2}\sum_{\alpha\neq\beta} P_\alpha^2 P_\beta^2\right), \tag{5.10}$$

which may be important in soft, highly-polarizable, lattices because ω_0 is then small. The quasi-harmonic approximation has been used[96] to show that, when $T \gtrsim T_c$, anharmonism can be approximately taken into account by renormalizing the lattice permittivity by an amount ε_l which satisfies the following equation near T_c:

$$\left(\frac{\varepsilon_0}{\varepsilon_l}\right)^{3/2} - \left(\frac{\varepsilon_0}{\varepsilon_l}\right)^{1/2} = \Lambda, \quad \Lambda \propto \frac{bnd^2\varepsilon_0^3}{r_c^3}, \quad b = b_1 + \frac{2}{3}b_2. \tag{5.11}$$

For slowly reorienting dipoles ($\nu \ll \omega_0$), the quantity ε_l has a clear physical meaning: it is the permittivity of the lattice at frequencies $\omega \gg \nu$, which has been renormalized by the dipoles. For $\nu \ll \omega_0$, equation (5.11) is thus seen to reflect the effect of the quasi-static dipole fields on the lattice which, because of anharmonism, are found to increase the soft-mode frequency $\Omega \propto 1/\sqrt{\varepsilon_l}$ of the crystal containing impurities as compared with the result $\omega_0 \propto 1/\sqrt{\varepsilon_0}$ for the pure crystal. This leads, in particular, to a weaker concentration dependence of the phase transition temperature. Thus, for $\Lambda \gg 1$, we have $T_c \propto n^{1/3}$, in contrast to the square root[96] in (5.6).

Anharmonic effects are much stronger for $T \ll T_c$ (much lower ε_0^{-1}). They determine, in particular, the magnitude of the impurity-induced spontaneous polarization which, for example, for $\mathbf{d} \parallel [100]$ satisfies the equation[97]

$$\frac{4\pi}{\varepsilon_0}P_\alpha + b_1 P_\alpha^3 + b_2 P_\alpha \sum_{\beta\neq\alpha} P_\beta^2 = \frac{4\pi\gamma dn}{3}\frac{\operatorname{sh}(4\pi\gamma d P_\alpha/3kT)}{\sum_{\alpha'}\operatorname{ch}(4\pi\gamma d P_{\alpha'}/3kT)}. \tag{5.12}$$

The solution of (5.12) shows that for $T \ll T_c$, and in contrast to the ordinary phase transitions, the direction of the domains is practically independent of the ratio of the coefficients b_1 and b_2 and is parallel to the possible dipole orientations. However, the situation may be different for $T < T_c$ for which the expansion of the right-hand side in powers of P is valid. Hence the direction of spontaneous polarization may change as the temperature is reduced.

The dependence of saturation polarization on dipole concentration is also found to exhibit a characteristic singularity. It is clear from (5.12) that, for low concentrations, this dependence is nearly linear, but then approaches $n^{1/3}$.

(d) Type of phase transition

When only the electric dipole moment of an off-center ion is taken into account, the result is a type II ferroelectric phase transition. It has been shown,[98] however, that the transition type may change when the off-center ion interacts strongly enough with other deformations, i.e., if it has a substantial elastic moment as well. The off-center ion then interacts simultaneously with polarization and lattice deformation, and this leads to the appearance of an additional temperature-dependent electrostriction term in the free energy of the crystal. The corresponding electrostriction coefficient is

$$\Delta q \propto \frac{gnd^2}{(kT)^2}, \tag{5.13}$$

where g is the interaction constant between the off-center ion and the elastic deformations. Since electrostrictional inter-

actions always reduce the anharmonic constants b_1 and b_2, and Δq increases as the temperature is reduced, it is possible for the coefficient b_1 to vanish for $T = T_1 > T_c$, and to become negative for $T < T_1$. The phase transition will then exhibit the features of a type I phase transition, with temperature dependent anharmonic constants.

(e) Dynamic susceptibility

If the motion of the dipole is determined by thermal reorientations between different positions of equilibrium, it may be considered that their single-particle distribution function ρ_i satisfies the kinetic equation

$$\frac{\partial \rho_i}{\partial t} = -\nu(\rho_i - \rho_i^{eq}), \tag{5.14}$$

which describes the relaxation of dipoles to the quasi-equilibrium Boltzmann distribution

$$\rho_i^{eq} = \exp\left(\frac{4\pi\gamma \mathbf{d}_i \mathbf{P}(r_i)}{3kT}\right)\left[\mathrm{Sp}\exp\left(\frac{4\pi\gamma \mathbf{d}_i \mathbf{P}(r_i)}{3kT}\right)\right]^{-1} \tag{5.15}$$

for each instantaneous $P(r,t)$. This approximation is analogous to the well-known Ising model[99] which is valid near the phase transition temperature when the fluctuations in $P(r,t)$ slow down critically.

When the permittivity is determined with allowance for (3.2), (5.10), and (5.17), the result is[97]

$$\varepsilon_{\alpha\alpha}(\omega) = \frac{\varepsilon_0 \omega_0^2}{\Omega_\alpha^2 - \omega^2 - [\nu\delta_\alpha^2/(i\omega + \nu)]}; \tag{5.16}$$

where Ω_α is the soft-mode frequency in a crystal containing impurities (in the low-temperature phase, Ω_α splits and assumes two values) and $\delta_\alpha^2 \propto \langle d_\alpha^2 \rangle - \langle d_\alpha \rangle^2$, where the angle brackets represent thermal averaging.

Expression (5.16) corresponds to the susceptibility of the damped oscillator with memory, which is frequently used as a phenomenological model of the soft mode in the interpretation of experimental data.[75,100] In our case, memory arises because at high frequencies, the dipoles do not succeed in reorienting in the rapidly varying local field. For $\omega_0 \gg \nu$, the fluctuation spectrum $I(\omega) \propto \omega^{-1}\varepsilon''(\omega)$ contains a peak at zero frequency, whose width is approximately given by

$$\Gamma = \nu\tau. \tag{5.17}$$

The appearance of this central peak in systems with reorienting impurities was first discussed in Ref. 95.

We also not that, since $\omega_0 \gg \nu$, the polarization of the crystal follows adiabatically the values of the dipole moment, and the phase transition under investigation is a transition of the order-disorder type.

(f) Local fluctuations. Effects in ESR and NMR

To analyze fluctuation effects, we must know the polarization fluctuation function $\langle \mathbf{P}(\mathbf{r},t)\mathbf{P}\rangle_{q\omega}$. According to (3.3),

$$\langle \mathbf{P}(\mathbf{r}, t)\mathbf{P}\rangle_{\mathbf{q}\omega} \propto \hat{K}_{\mathbf{q}}\hat{S}_{\mathbf{q}\omega}\hat{K}_{-\mathbf{q}}, \tag{5.17'}$$

where $\hat{K}_{\mathbf{q}}$ are the Fourier components of the matrix $\hat{K}(\mathbf{r})$ (3.4) and $S_{q\omega}$ is the dynamic structure factor describing correlations between the orientations of different dipoles:

$$\hat{S}_{\mathbf{q}\omega} = n\langle d_i^*(t)\, d_i^*\rangle_\omega + n^2\langle d_i^*(t)\, d_j^*\rangle_{\mathbf{q}\omega}. \tag{5.18}$$

The factor $S_{q\omega}$ was calculated in Ref. 96 in the random-phase approximation by analogy with the dynamic Ising model.

Let us begin by considering the spectrum of static fluctuations. When $T \gtrsim T_c$, we have[96]

$$\langle P_\alpha(r) P_\beta\rangle_q = \frac{\varepsilon_0}{4\pi}\frac{kT_c}{V}\frac{\delta_{\alpha\beta} - (q_\alpha q_\beta/q^2)}{\tau + r_c^2 q^2}\frac{1}{1 + r_c^2 q^2}. \tag{5.19}$$

The characteristic feature of (5.19) as compared with the situation in ordinary phase transitions is the presence of the additional factor $(1 + r_c^2 q^2)^{-1}$. This leads to a rapid damping of the correlator (5.19) already for wave vectors $q \gtrsim r_c^{-1}$, i.e., the Fourier components of fluc.uations with $q \gtrsim r_c^{-1}$ turn out to be effectively cut off, so that the fluctuation spectrum is highly smoothed, since in soft lattices $r_c > a$.

This smoothing does not affect the behavior of the extreme long-wavelength critical Fourier components of the fluctuations, but it does affect the mean square fluctuation in $\langle P_\alpha P_\beta\rangle$, since it produces an increase in the relative contribution of critical Fourier components to $\langle P_\alpha P_\beta\rangle$.

Since the mean square value of local fluctuations can be determined directly by measuring the ESR line broadening, let us consider in somewhat greater detail the properties of this broadening near T_c.

The critical slowing down of fluctuations near T_c ensures that the broadening is quasi-static but, in contrast to Section 4b, where the different dipoles were assumed to contribute independently to the broadening, the effects of dipole correlations due to the interaction (3.5) must now be taken into account near T_c. The statistical theory of line shape[74] is then invalid, but the situation is simpler because, near T_c, the line shape is approximately Gaussian in the region in which the random-phase approximation used in deriving (5.19) is valid.

The linewidth δ is then determined by the second moment M_2 ($\delta \approx 2.36\sqrt{M_2}$) which, according to (4.2), is proportional to the mean square local fluctuation:

$$M_2 \propto \langle P^2\rangle, \tag{5.20}$$

or, using (5.19),

$$M_2(T) \propto M_2(T_c)\frac{1}{1 + \sqrt{\tau}}. \tag{5.21}$$

This temperature dependence of the linewidth near T_c reflects the increased contribution of the critical long-wave Fourier components of the fluctuations.

Temporal fluctuations in polarization, leading to a time dependence of $\Delta\omega$ in (4.2), may become important for $T > T_c$. In the limit of rapid fluctuations, the static profile narrows, and we have the Lorentzian profile of width

$$\lambda = \int_{-\infty}^{\infty} dt\,\langle \Delta\omega(t)\,\Delta\omega\rangle \propto \int_{-\infty}^{\infty} dt\,\langle P(t)\,P\rangle. \tag{5.22}$$

According to Ref. 96,

$$\lambda \propto M_2\frac{1}{\nu\sqrt{\tau}}. \tag{5.23}$$

It is clear from this that dynamic narrowing does indeed occur not too close to T_c, since the condition $\lambda < \sqrt{M_2}$ must be satisfied.

It is also clear from (5.23) that, by measuring the ESR linewidth in the region of the dynamic narrowing, we can determine the frequency ν and hence, using (5.17), the width Γ of the central peak.[101]

The rate of nuclear spin-lattice relaxation of the off-center ions due to modulation of intracrystalline fields by the reorientation of ions has also been calculated.[96] The relaxation rate W is proportional to the correlation function of the square of the local fluctuation $\langle P^2(t)P^2\rangle_{\omega z}$ (ωz is the resonance frequency) and has the following logarithmic critical singularity near T_c:

$$W \propto -\frac{1}{18\pi^3 n^2 r_c^6 \nu} \ln \tau. \tag{5.24}$$

(g) Comparison with experiment

Finally, let us compare the consequence of the theory with the experimental data on $K_{1-x}Li_xTaO_3$ and $Pb_{1-x}Ge_xTe$. First, we note that, since the concentrations of off-center ions were sufficiently high in these experiments ($x > 1\%$) and $r_c \approx 2a$–$3a$, the necessary condition for the validity of the mean-field approximation, i.e., $nr_c^3 \gtrsim 10^{-1}$, is satisfied.

To begin with, consider $KTaO_3$:Li. Formula (5.6) provides a good description of the experimental concentration dependence of the phase transition temperature (cf. Fig. 14), which is close to $T_c \propto \sqrt{x}$. A qualitative explanation of the concentration and temperature dependence of the residual polarization (cf. Fig. 13) is provided by (5.12) if this polarization is identified with the spontaneous polarization in a specimen in which a single-domain state is produced by the electric field. The theory will also explain the splitting of the soft-mode frequency below T_c and its finite value for $T = T_c$, which indicates an order-disorder type transition.

Inclusion of the interaction between off-center ions and elastic lattice deformations has enabled us to understand why the phase transition has the features of a type I transition with temperature dependent anharmonic coefficients, and has exposed the nature of the unusual behavior of the nonlinear dielectric response.

The absence of anomalies in the rate of spin-lattice relaxation of Li nuclei should now be clear in the light of the foregoing discussion, since it follows[96] from (5.24) that we cannot expect appreciable manifestations of critical anomalies in the rate of relaxation within the experimentally attained[44] temperature range near T_c. This was not understood at the time by the authors of the experiment.

The nature of the additional low-frequency dispersion of permittivity and of the small randomly oriented domains is still partly unclear. It is possible that these two phenomena are due to the presence of two closely spaced Li^+ dipoles.[27] Such closely spaced dipoles produce an additional barrier for mutual dipole reorientation, and therefore have long relaxation times that lead to the low frequency dispersion of permittivity in the high-temperature phase. When the temperature is reduced, and the relaxation time becomes longer still, the closely spaced pairs behave like static defects which should[102] fix the random directions of the domains.

The theory of the ferroelectric phase transition induced by off-center ions has been used[60] to explain some of the properties of $Pb_{1-x}Ge_xTe$. It was shown that good agreement with experiment can be achieved for the concentration dependence of the phase transition temperature, the temperature dependence of the permittivity, and the temperature dependence of the tetrahedral lattice distortion angle (cf. Figs. 17–19).

The theory of the ferroelectric phase transition induced by off-center ions is thus seen to be in good agreement with the observed physical properties of $KTaO_3$:Li and PbTe:Ge.

6. CONCLUSIONS

We have tried to show that crystals containing off-center ions are very promising objects for the investigation of cooperative phenomena in disordered systems of dipolar particles. The principal feature of such systems is the definite form of the interaction potential, which has been responsible for the qualitative success of the theory.

Some of the conclusions relating to the behavior of systems containing off-center ions will probably be useful in the investigation of spin and structural glasses[103] in which the situation is greatly complicated by the presence of different types of interaction. In particular, in spin glasses, the role of magnetic dipole-dipole interactions has not as yet been definitely settled.[104]

Of particular interest are investigations of highly-polarizable crystals containing off-center ions in which, at low temperatures, there should be a concentrational phase transition from a dipole glass to a ferroelectric. It is clear that the system will exhibit different properties near the critical concentration, as compared with the "classical" dipole glass or the disordered ferroelectric.

However, so far, only the first steps have been taken both in theory and in experiment, and a sufficiently detailed analysis has been performed only of the validity of the mean-field approximation.

Moreover, no instances have been reported in which the concentrational phase transition has been produced experimentally by continuously increasing the concentration of dipoles. In the case of $KTaO_3$:Li, this is prevented by the necessity for low temperatures (below 30 K) at which the presence of the high potential barrier ensures that thermal motion is completely frozen out even for Li ions isolated from one another. In the case of PbTe:Ge, the impeding factor is the high tunneling frequency, which ensures that the dipole-dipole interaction is ineffectual as the concentration of Ge is reduced.

Experimental studies involving systematic searches for off-center ions in highly-polarizable crystals would therefore be very desirable.

In conclusion, the authors wish to express their indebtedness to V. L. Ginzburg for his stimulating interest in the subject of this review and also to A. P. Levanyuk for useful suggestions.

[1)]We note, however, that the very phrase "spin glass" is as yet not entirely unambiguous. It is sometimes understood to designate only a particular

"nonergodic state" for which the relaxation time tends to infinity when the linear dimensions of the sample tend to infinity. This contrasts, for example, with ordinary glasses for which the relaxation time is a characteristic of the material. There is as yet no experimental confirmation of this nonergodicity of dipole systems. When we refer to a "dipole glass" we shall therefore understand this to mean a simple analogy with systems of randomly distributed spins, the interaction potential between which can change sign. In most papers, such systems are referred to as "spin glasses."

[2)]However, this restriction is not at all necessary when we consider the static and quasi-static behavior of impurity dipoles in highly-polarizable lattices, and the validity of the foregoing results is actually restricted only by the condition that the transverse optical strength of the pure crystal is low.

[3)]We emphasize that (3.3) correctly describes the static properties of the system whatever the ratio of ν to ω_0.

[4)]We note that the random molecular field method used in these calculations does not allow us to monitor the precision of the calculated critical concentration. However, the application of this method to the well-known problem of the percolation of "spheres" (short-range interaction; cf., for example, Ref. 39) has shown that the error introduced by this method does not exceed 50%. On the other hand, for long-range potentials, it may be expected that the uncertainty in the calculated critical concentration should be substantially lower.[27]

[5)]We have in mind here the values of the local field at equivalent lattice points for which the parameter γ has the same value.

[6)]The coefficient in the term $(1/4)b_1P^4$ in the free energy of the crystal.

[7)]The condition $B(T_c^*) = 0$ gives an independent estimate of the critical concentration $n_{cr}r_c^3 \approx 10^{-2.94}$. It is in agreement with the discussion of the low-temperature region.

[8)]Although the discussion in Ref. 95 was concerned with nondipolar impurities near nonferroelectric structural phase transitions, the dipolar nature of the impurities is not important in the region of validity of the mean-field approximation (i.e., for large enough nr_c^3), since according to (5.2) the phase transition temperature does not depend on the anisotropic "dipole" terms in the interaction Hamiltonian (3.4) of the dipole impurities, but is determined only by the Ornstein-Zernike part of the interaction $V \sim \exp(-r/r_c)$, which is universal for all impurities in soft lattices.

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