Superionic phase transition in crystals of the $(NH_4)_2SbF_5$ type

W. Urbanovitschyus, V. E. Schneider, J. P. Grigas, and T. L. Dawidowich

Institute of Semiconductor Physics, Lithuanian Academy of Sciences
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The temperature dependences are investigated of the complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ and of the electric conductivity σ in M_2SbF_5 crystals, where M = Na, K, Cs, and NH_4. Phase transitions of the order-disorder type, near which ε', ε'', and σ have anomalies, have been observed. An analysis of the results shows that the phase transition is due to disordering of the fluorine ion, and that a transition into the superionic state takes place, at least in $(NH_4)_2SbF_3$. The experimental results are qualitatively explained on the basis of the Potts q-component model with nonmagnetic impurities, within the framework of the molecular-field approximation.

1. INTRODUCTION

Several families of superionic crystals, whose high conductivity is due to motion of fluorine ions, are known by now. These include, for example, crystals such as CaF_2, LaF_3 (Ref. 1) and $MBiF_4$ (M = K, Rb, Tl).[2] An extensive program of experimental research into these compounds[1,3] has shown that in the vicinity of a first-order (LaF_3) or a second-order (CaF_2) phase transition the second derivatives of the thermodynamic functions (e.g., the heat capacity), behave anomalously. At the same time, one of the most important properties of the system, namely the dielectric constant ε of the medium, has no anomalous behavior. This raised the question whether this behavior of ε is a characteristic property of superionic compounds or whether more objects must be studied to observe anomalies of ε, the more so since no anomalies of ε were observed also in other crystals whose ionic conductivity is due to motion of another type of carrier—Ag, Cu, K, Cs, and others.[1,3] Only recently[4] was an increase of ε observed in the Li_3N crystal near the temperature of the transition into the disordered state.

We have investigated in the present study the behavior of various macroscopic quantities in the family of M_2SbF_5 crystals with M = Na, K, Cs, and NH_4, where an anomalous increase of ε was observed in preliminary measurements.[5]

This choice of objects for the investigation was not accidental. Trivalent antimony forms numerous complex fluorides. A feature of their stereochemistry is constancy of the coordination number of the central atoms, inequality of the bonds, and a tendency to produce chainlike and layered structures. The complex anions form infinite chains. All this leads to distortion and to "loose" low-symmetry lattices, making these compounds good candidates for various phase transitions, including superionic ones.

In Sec. 2 we discuss the distinguishing features of the crystal structure of the M_2SbF_5 family and present the results of experimental investigations of the complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ and of other macroscopic characteristics in the vicinity of the phase transition. In Sec. 3 we introduce the Potts q-component model, whose solution in the molecular-field approximation explains qualitatively the experimental data.

2. STRUCTURE OF CRYSTALS AND EXPERIMENTAL RESULTS

Antimony trifluoride forms a large number of complex compounds with alkali-metal fluorides. The compounds M_2SbF_5 (M = K, Rb, Cs, NH_4) crystallize in a rhombic syngony (space group $Cmcm$) and form an amorphous sequence.[6,7] The M_2SbF_5 structures are made up of the complex ions $[SbF_5]^{2-}$ ions and M^+ ions. The anion configuration of the $[SbF_5]^{2-}$ anion takes the form of a distorted octahedron, in which one of the six vertices is occupied by an undivided pair of s electrons. A similar anion structure was found in Na_2SbF_5 (space group $P2_12_12_1$) (Ref. 8). The structure "hole" containing the undivided pair of electrons is surrounded in one plane by an antimony atom and three nitrogen atoms.[7] Thus, the structure of an M_2SbF_5 compound has channels in which the F^- ions can move easily when they become temperature-disordered in an electric field.

The M_2SbF_5 crystals were grown by evaporation of the solvent from a saturated aqueous solution at room temperatures.

The components of the complex low-frequency dielectric tensor were measured with a bridge or with a Q meter, while the measurements at microwave frequencies were made by the procedure of Ref. 9. The dc conductivity was determined with an electrometric amplifier. The measurements were made in a vacuum cryostat. We used electrodes of aquadag, silver paste, and gold sputtered in vacuum.

The dielectric constant of the crystals of the M_2SbF_5 family. At 1 kHz and $T = 290$ K we have for Na_2SbF_5 $\varepsilon_a' = 3.8$, $\varepsilon_c' = 3.3$, $\varepsilon_b' = 11$; $\varepsilon_a'' = 1.3$, $\varepsilon_b'' = 1.4$, $\varepsilon_c'' = 0.28$; for K_2SbF_5 $\varepsilon_a' = 6.7$, $\varepsilon_c' = 4$, $\varepsilon_b' = 10.5$; $\varepsilon_a'' = 0.04$, $\varepsilon_c''= 0.03$, $\varepsilon_b'' = 0.14$; and for Cs_2SbF_5 $\varepsilon_a' = 3.0$, $\varepsilon_c' = 3.5$, $\varepsilon_b' = 10$; $\varepsilon_a'' = 0.18$, $\varepsilon_c'' = 0.19$, $\varepsilon_b'' = 0.53$. At 10 GHz the dielectric parameters are close to those at low frequencies.[5] The parameters ε_a', ε_c' and ε_a'', ε_c'' are practically independent of frequency and temperature. The contribution of the ionic polarization $\Delta\varepsilon_j$ to the dielectric constant of the same order as that of the electronic
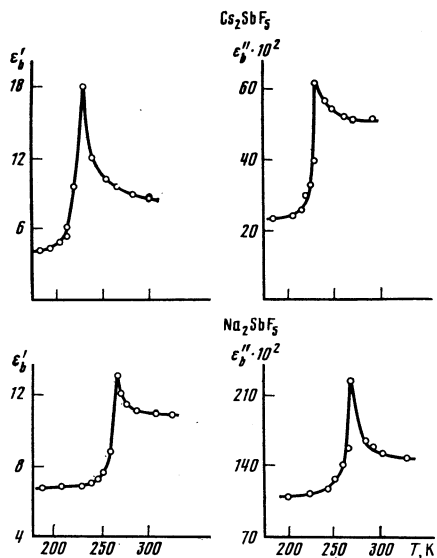
FIG. 1. Dependence of the real (ε_b') and imaginary (ε_b'') parts of the complex dielectric constant of the crystals Cs_2SbF_5 and Na_2SbF_5 on the temperature at the frequency 1 kHz.

$\Delta\varepsilon_e$. For example, for Na_2SbF_5 only $\Delta\varepsilon_j = 4.55$ and is double the value $\Delta\varepsilon_c = 2.15$ (Ref. 10), while for the other components $\Delta\varepsilon_j \approx \Delta\varepsilon_e$.

However, the parameters ε_b' and ε_b'' of all the crystals of this family have temperature anomalies. Figures 1 and 2 show the temperature dependences of ε_b' and ε_b'' of the crystals Cs_2SbF_5, Na_2SbF_5 and $(NH_4)_2SbF_5$ at 1 kHz. With increasing frequency, in the range 10^3–10^{10} Hz, the anomalies of ε_b' and ε_b'' decreases and practically vanish already at 10^8 Hz, i.e., a considerable relaxational dispersion of the dielectric constant takes place in the 10^3–10^8 Hz range. The anomalies of ε_b' and ε_b'' were investigated in greatest details in Cs_2SbF_2 and $(NH_4)_2SbF_5$, but only in high-grade specimens is good reproducibility of the results obtained. Nonetheless, in these crystals there is no polarization mechanism that
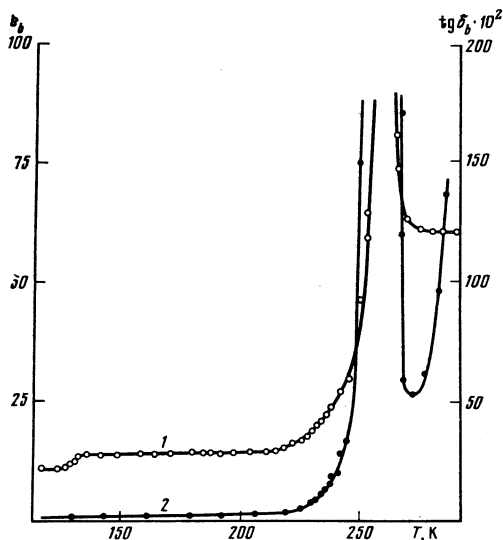
depends strongly on temperature, there are no anharmonic soft modes, and no spontaneous polarization is observed. Although in polarized Cs_2SbF_5 crystals at $E = 0$ there is generated a current that reveals[5] an anomaly with increasing temperature and reverses direction, depending on the polarity of the field, it is more readily thermo-ionic than a pyrocurrent. We did not succeed in observing dielectric-hysteresis loops in these crystals in electric fields $E < 3$ kV/cm. In stronger fields the crystal goes over into a low-resistance state.[5] X-ray diffraction measurements of Cs_2SbF_5 with a DRON-2, 0 diffractometer in $CuK\alpha$ radiation have shown that the dielectric anomaly is connected with a small change in the structure without a change in the crystal symmetry.

Jumplike anomalies of the complex dielectric constants were observed also in more complicated fluorides of antimony of the type $M_6Sb_4(SO_4)_3F_{12}$, where M $=$ Rb or NH_4 (Ref. 11), in which structural investigations have confirmed the occurrence of phase transitions without change of symmetry.

It is known that the electric conductivity of fluorides is most frequently due to mobile F^- ions. A determination of the ionic part of the electric conductivity of $(NH_4)_2SbF_5$ by the Yokota method[12] has shown that it constitutes more than 90% at 290 K, i.e., the electric conductivity is mainly ionic. At 290 K the electric conductivity in an electric field up to 100 V/cm is 1×10^{-10}, 5×10^{-10}, and 2×10^{-8} Ω^{-1}/m for Na_2SbF_5, K_2SbF_5, and Cs_2SbF_5, respectively. In the temperature region of the dielectric anomalies, the electric conductivity changes jumpwise.[5] The strongest jump takes place in $(NH_4)_2SbF_5$ crystals, for which the ac conductivity σ_ω at 10 kHz along the b axis is 1.5×10^{-5} Ω^{-1}/m at room temperature. On the linear part of the current-voltage characteristic at room temperature, the conductivity along the a-axis direction is $\sigma_a = 3.5 \times 10^{-9}$ Ω^{-1}/m and increases exponentially with temperature, with activation energy $E_a = 0.72$ eV. The temperature dependence of σ along the b axis is shown in Fig. 3. When the crystal is heated to in an external field the crystal goes over in the dielectric-anomaly temperature region into
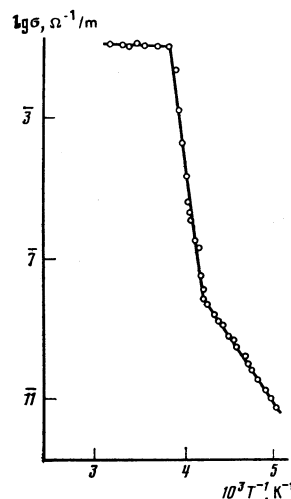

FIG. 2. Temperature dependences of ε_b' (1) and of $\tan \delta_b$ (2) of the crystal $(NH_4)_2SbF_5$ at 1 kHz.

FIG. 3. Temperature dependence of the electric conductivity of the crystal $(NH_4)_2SbF_5$.

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a conducting state in which it remains for several days or weeks, and in which σ is practically no longer temperature-dependent. The conductivity jump increases in this case by 10^6–10^7 times. A change in the conductivity jump by 10^3–10^4 times takes place also along the c-axis direction. We note that a temperature change in the absence of the field E does not make the crystal conducting.

At $T = 258$ K the heat capacity of powdered $(NH_4)_2SbF_5$ experiences a jump of ≈ 10 J/mol·K. At this temperature a small inflection appears on the plot of the NQR frequencies vs temperature, whereas the line widths in the NMR spectra change jumpwise.

The foregoing experimental results show that distortion phase transitions of the order–disorder type take place in crystals of the M_2SbF_5 family and are due to the disordering of the anion sublattice. The nature of the phase transitions is apparently the same for all the compounds mentioned above, and the results cited in Ref. 3 show that the phase transition in $(NH_4)_2SbF_5$ can be classified as superionic.

3. THEORY

It follows from the analysis of the experimental data that with increasing temperature the fluorine ions in the M_2SbF_5 crystals leave the regular site positions and go into interstices, while the M and Sb ions remain in their places. The theory of superionic phase transition based on the assumption that one of the sublattices is disordered was developed by many workers.[13-17] Thus, a phenomenological theory of the transition was developed in Refs. 13, 14, and 16 by starting from the model of interacting Frenkel defects. In Ref. 15, using a microscopic Hamiltonian within the framework of the quasichemical approximation, they investigated the behavior of the basic thermodynamic functions in crystals of the CaF_2 type. At the same time, problems connected with the possible onset of dielectric anomalies in the vicinity of the superionic transitions were not considered in Refs. 13–16. In Ref. 17, however, a theory that explains the presence of these anomalies was constructed. But the Onsager model used in Ref. 17, which describes accurately enough a solution of dipole molecules in a nonpolar liquid, is apparently somewhat oversimplified for crystals. In particular, it is proposed in Ref. 17 that if the number of interstices is infinitely large, a dipole of the "site–interstice" type appears in the system and has an arbitrary direction in space. Yet in real crystals the number of directions of a dipole, if it exists at all, should be limited by anisotropy, by particle-blocking effects in the interstices, and by the lattice symmetry. The number z_{is} of interstices per number z_s of nonequivalent sites in the cell does not always exceed unity considerably. For example, $z = z_{is}/z_s$ is equal to 21/2, 4, 23/8, 3/2, and 1/2 in Ag_2S, CuI, $RbAg_4I_5$, α-Li_2SO_4, and CaF_2, respectively.[3]

In this section we consider a model that makes it possible to generalize the earlier theories[13,14,16,17] and explain qualitatively the presence of dielectric anomalies in a superionic transition.

The gist of our model is the following. If the ions are in sites, their "shape" differs little from spherical and the average dipole moment of an ion is zero. A move to the interstices increases the polarizability of the medium and the spherical geometry of the mobile ion can change. As a result it acquires an effective dipole moment that has, generally speaking, q directions in space. There are as yet no experimental data to confirm the above for the M_2SbF_5 crystal. However, an analysis of neutron diffraction and x-ray diffraction patterns for several superionic crystals shows[3] that the spherical "shape" of the ions in the interstices does become distorted. It is therefore reasonable to propose a similar picture also for M_2SbF_5.

The interaction potentials between ions located in interstices $\mathbf{r}$ and $\mathbf{r}'$ consist of "exchange" $J_{ik}(\mathbf{r} - \mathbf{r}')$ and non-exchange $V_{ik}(\mathbf{r} - \mathbf{r}')$ parts, while the potentials of interactions of the site–site and site–interstice type have only non-exchange parts. If the dipoles are parallel, then $J_{ik} = J_{ik}^{(1)}(\mathbf{r} - \mathbf{r}')$, while in all the remaining cases $J_{ik} = J_{ik}^{(2)}(\mathbf{r} - \mathbf{r}')$. We express the Hamiltonian of the system in the form

$$\mathcal{H} = -\frac{1}{2} \sum_{\substack{i,k \\ r,r'}} \eta_r{}^i \eta_{r'}{}^k [J_{ik}(\mathbf{r}-\mathbf{r}')\delta_{r_m r_{i'}} + V_{ik}(\mathbf{r}-\mathbf{r}')]$$
$$+ \sum_{i,r} \Delta_i \eta_r{}^i - E \sum_{i,r} \eta_r{}^i p_i \delta_{r_m \, 1}, \tag{1}$$

where $\delta_{\mathbf{r}\mathbf{r}'}$ is the Kronecker symbol or, in other words, the matrix of the Potts q-component model,[18] E is the external electric field, p_i is the effective dipole moment of an ion in a site ($i = 2$, $p_2 = 0$) and in an interstice ($i = 1$). The quantity η_r^i describes the distribution of the ions over the sites and interstices. The mean values $\langle \eta_r{}^2 \rangle = c_2$ and $\langle \eta_r{}^1 \rangle = c_1$ over the lattice are the densities of the ions in the sites and interstices, respectively; Δ_i is the energy ($\Delta_2 = 0$, $\Delta_1 > 0$) of the transition of a particle from a site to an interstice.

We note that Hamiltonian (1) at $q = 2$ (corresponding to the Ising model) and $\Delta_i = 0$ was used earlier to describe phase transitions in solid solutions[19] and in clathrate inclusion compounds.[20] The problem of phase transitions in a superionic compound has thus been reduced to the problem of investigating the Potts q-component model with nonmagnetic impurities in an external field. To bring to light the qualitative features of the behavior of the macroscopic quantities we confine ourselves to the molecular-field (MF) approximation. We define

$$\delta_{\xi\xi'} = \frac{1}{q} \sum_{k=1}^{q} \xi^k (\xi')^{q-k}, \tag{2}$$

where $\xi = 1, \omega, \omega^2, \ldots, \omega^{q-1}$ with $\omega = \exp(2\pi i/q)$, and introduce the mean value of the "spin" $s = \langle \xi \rangle$ (Ref. 18). The expression for the free energy F per mobile ion then takes in the MF approximation the form

$$F - F_0 = Ac^2 - Bc^2 - \frac{q-1}{2q} Ks^2 c^2 - \frac{q-1}{q} pEsc$$
$$+ T[-z \ln z + 2c \ln c + (1-c)\ln(1-c) + (z-c)\ln(z-c)]$$
$$+ \frac{Tc}{q} \{[1+(q-1)s]\ln[1+(q-1)s] + (q-1)(1-s)\ln(1-s) - q\ln q\}. \tag{3}$$

Equation (3) takes into account the fact that

$$J_{ik} = \sum_{r} J_{ik}(r), \quad V_{ik} = \sum_{r} V_{ik}(r),$$

$J_{12} = J_{22} = \Delta_2 = p_2 = 0$, $c_1 + c_2 = 1$, and makes use of the notation

$$K = J_{11}^{(2)} - J_{11}^{(1)}, \quad c = c_1, \quad \Delta' = \Delta_1, \quad p = p_1,$$

$$A = V_{22} + \Delta - V_{12}, \quad B = \tfrac{1}{2}(V_{11} + V_{22}) - V_{12}. \tag{4}$$

For all the sites to be occupied as $T \to 0$ ($c(T = 0) = 0$), we must have $A > B$ or $V_{22} > V_{11} - 2\Delta$. The consistency equation for the determination of the equilibrium values of s and c take the form

$$s = \frac{1 - e^{-\beta\alpha}}{1 + (q-1)e^{-\beta\alpha}}, \tag{5a}$$

$$\beta\left(A - 2Bc - \frac{q-1}{q}\alpha s\right) + \ln\frac{c^2}{(1-c)(z-c)} + \frac{1}{q}\{[1 + (q-1)s]$$
$$\times \ln[1+(q-1)s] + (q-1)(1-s)\ln(1-s) - q\ln q\} = 0, \tag{5b}$$

$$\alpha = Ksc + pE, \quad \beta = T^{-1}.$$

We note that at $q = 2$ and $z = 1$ relations (5) go over into the results of Refs. 19 and 20. Equations (3)–(5) determine the thermodynamics of the system, expressing s and c in terms of the parameter of the model. For the dielectric constant ε we thus obtain from (5a) ($\varepsilon = \varepsilon_0 + c4\pi p v_c^{-1} ds/dE$)

$$\varepsilon = \varepsilon_0 + ecq\{T[(q-1)e^{-\beta\alpha/2} + e^{\beta\alpha/2}]^2 - qKc\}^{-1}, \tag{6}$$

where $e = 4\pi p^2/v_c$ and v_c is the volume per mobile ion.

Two types of phase transition can occur in the system described by relations (3)–(6), viz., ferroelectric ordering ($s \neq 0$) at the point

$$T_c = Kc(q-2)/2(q-1)\ln(q-1) \tag{7}$$

and "ionic" ordering with respect to the concentration c. The experimental data, however, indicate that no state with $s \neq 0$ is realized in superionic conductors. We shall assume therefore that the "ionic" ordering takes place in the paramagnetic phase ($s = 0$), and shall not discuss here questions connected with phase transitions into the ferroelectric state. Equation (5b) and the formula for ε at $E = 0$ take the simple forms

$$c^2/(1-c)(z-c) = \exp[-\beta(A-2Bc)], \tag{8a}$$

$$\varepsilon = \varepsilon_0 + ce/(Tq - Kc). \tag{8b}$$

We note that from (8b) at $q = 2$ and $K = 0$ follows the Langevin-type formula used in Ref. 17. An analysis of expressions (3) and (8) shows that when T is lowered, a superionic first-order phase transition takes place at the point

$$T_{\mathrm{ord}} \approx (V_{22} + 2\Delta - V_{11})/2(1 + \ln z)$$

from the state with $c \approx 1$ to the state with $c \approx 0$. In this case $T_{\mathrm{ord}} > T_c > T_0 = Kc/q$.

If $p = K = 0$ the relation (8a) is equivalent to the results of Ref. 14, where the $c(T)$ dependences were investigated quite in detail in various ranges of the parameters A and B. Therefore, without dwelling on this, we proceed to investigate the $\varepsilon(T)$ dependence near T_{ord}. As seen from (8b), $\varepsilon(T)$ is determined by three parameters: $c(T)$, K, and q. If $T_{\mathrm{ord}} \gtrsim cK/q$ and the density has a discontinuity at $T = T_{\mathrm{ord}}$, the quantity $\Delta\varepsilon = \varepsilon - \varepsilon_0/e$ also changes jumpwise. Figure 4 shows a
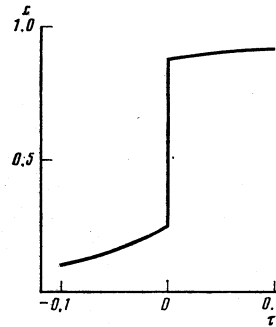

FIG. 4. Temperature dependence of the density c of the ions in the interstices at $A/2B = 0.99$ and at $z = 8$.

plot of c vs $\tau = (T - T_{\mathrm{ord}})/T_{\mathrm{ord}}$ which is most typical of superionic crystals. The resultant plot of $2\Delta\varepsilon$ at $q = 2$ and at various values of K is shown in Fig. 5. With increasing K the plot of $\Delta\varepsilon(\tau)$ becomes more peaked at $\tau > 0$, but $\varepsilon(\tau = 0)$ does not become infinite because of the restriction $T_{\mathrm{ord}} > T_c > T_0$. If $c(\tau)$ varies smoothly, $\Delta\varepsilon(\tau)$ also varies smoothly. When bitransitions[14] appear in the system, $\varepsilon(T)$ has discontinuities in the first and in the second transitions. It is interesting that if q is large enough and K is small, i.e., $T_{\mathrm{ord}} q \gg Kc$ and $e \gtrsim T_{\mathrm{ord}}$ (usually $e \sim 10^3$ K at $p \approx 0.1$–0.5 D), then $\varepsilon \approx \varepsilon_0$ independently of the size of the density jump. This case is apparently realized in those crystals in which there is no anomalous behavior of ε (for example, α-AgI, MeAg$_4$I$_5$, CaF$_2$ and others[3]). We note finally that the specific heat is

$$c_p(T) = T(\partial^2 F/\partial c^2)_{c=c_m}(\partial c/\partial T)^2,$$

where c_m is the equilibrium value of the concentration, experiences a jump at T_{ord}.

The described model thus explains qualitatively the onset of the anomalous behavior of ε and c_p near the superionic-transition point. Obviously, for a quantitative comparison with the experimental data on M$_2$SbF$_5$ crystals (see Figs. 1 and 2) we must use an approximation more accurate than that of the molecular field, say the cluster approximation.[21] To this end, however,
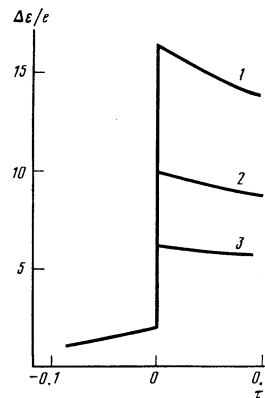

FIG. 5. Temperature dependence of the dielectric constant ε with $c(\tau)$ as indicated in Fig. 4 and at $q = 2$ for $K/2B = 0.2$ (curve 1), $K/2B = 0.12$ (curve 2), and $K = 0$ (curve 3). The positions of the curves below the transition are very close, therefore only one curve is indicated at $\tau < 0$.

it is necessary to carry out a large number of additional experiments, including an analysis of the M_2SbF_5 structure below T_{ord}.

We now compare our results with the earlier ones.[16,17] We put in Eqs. (3) and (5) $z = 1$, $q = 2$, and $K = 0$. Substituting then $s = \tanh(\beta pE/2)$ from (5a) in (5b), we obtain the relation given in Ref. 16:

$$c/(1-c) = \exp[-\beta(A-2Bc)]\,\mathrm{ch}(\beta pE/2), \qquad (9)$$

and discussed there in connection with the onset of a superionic state induced by an electric field E.

We put $V_{ik} = J_{ik} = 0$ and $\delta_{r1} = $ const in the Hamiltonian (1) (in which case E should be taken to mean the field determined by the polarization of the medium and calculated in Ref. 17 from the Onsager model). Assuming that $\eta_r^2 = 0$ and $\eta_r^1 = 1$ on z interstices we obtain from (1) the relation cited in Ref. 17

$$\langle\eta_r{}^1\rangle = c = e^{-\beta\Delta'}[1/z + e^{-\beta\Delta'}]^{-1},$$

with $\Delta' = \Delta_1 - p_1E(c)$. It must be noted that within the framework of the theory of Ref. 17 the dielectric constant ε must behave anomalously as soon as a superionic transition occurs in the system. In our model, however, when the number q of the dipole directions in the cell becomes large enough, we have $\varepsilon \approx \varepsilon_0 \approx$ const. Thus, chain and layer structures, such as M_2SbF_5, are the most suitable objects for the investigation of the dielectric anomalies connected with ionic disordering.

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