

trostatic potential of the converted wave. A center probe interferogram is shown at the bottom of Fig. 3 in parallel with the plasma absorption. In agreement with the resonance conditions, the absorption displays twice as many peaks as the potential at the plasma center. Various center probe interferograms are shown in Fig. 4. Note that resonances appear also for $\omega > 2\Omega_i$. Simultaneously, at a fixed magnetic field we measured with a movable probe the spatial interference corresponding to the wave. Various examples are given in Fig. 5. Short-wavelength waves are observed and their dispersion was measured, plotted in Fig. 5(b), and found to correspond to ion Bernstein waves. The fact that electrostatic waves are observed in the plasma core when $\omega > 2\Omega_i$ (see curves II and III in Fig. 5) is a consequence of the reflection of the outgoing converted wave in the low-density region. We observe in Fig. 4 an attenuation after reflection of the wave as compared to direct propagation when $\omega < 2\Omega_i$. The attenuation explains why no resonance is observed for the plasma absorption when $\omega > 2\Omega_i$. The attenuation itself can be explained as due to collisions during the wave-amplitude swelling at the reflection point and/or due to diffusion on drift wave turbulence, which is always present in the plasma periphery.

It is concluded that the present experiment gives clear experimental evidence of electromagnetic to electrostatic mode conversion at the lower hybrid layer. A second new observation is that, when the wave frequency is near a higher ion gyroharmonic ($\omega \sim n\Omega_i$; $n=3, 4, \dots$), the converted wave is observed to be reflected back to the high-density region of the plasma.

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¹T. H. Stix, Phys. Rev. Lett. **15**, 878 (1965); P. M. Bellan and M. Porkolab, Phys. Fluids **17**, 1592 (1974).

²R. R. Weynants, Phys. Rev. Lett. **33**, 78 (1974).

³S. J. Buchsbaum and A. Hasegawa, Phys. Rev. Lett. **12**, 685 (1964); for recent references see B. B. O'Brien and H. H. Khuel, Phys. Fluids **14**, 1187 (1971); F. Leuterer, Plasma Phys. **14**, 499 (1972).

⁴F. A. Rushworth and D. P. Tunstall, in *Nuclear Magnetic Resonance* (Gordon and Breach, New York, 1973), p. 61

⁵T. H. Stix, Phys. Fluids **1**, 308 (1958).

⁶J. P. M. Schmitt, Phys. Rev. Lett. **31**, 982 (1973).

New Kind of Phase Transition in Randomly Distributed Tunneling Dipoles in Alkali Halides

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We show that very dilute concentrations of dipole impurities distributed in alkali halides (for example, OH^- impurities in KCl) undergo a phase transition provided that the average impurity-impurity interaction is greater than the tunnel-splitting energy of a single dipole. This theory predicts a temperature-dependent cusp in the dielectric constant. The polarization in the absence of an applied field is predicted to be zero even below the transition temperature.

Dilute concentrations of OH^- impurities distributed in alkali halides were found by Kuhn and Luty¹ to form dipoles with six well-defined discrete orientations. A single dipole tunnels between the different orientations; the tunneling states have been examined by Bauer and Salzman,² Gomez, Bowen, and Krumhansl,³ and Shore.⁴ The calculations show²⁻⁴ that the degeneracy of the multiorientational states is removed by the tunneling matrix element and that the various levels are split into their respective tunneling states. Similar tunnel-

ing properties are observed for other impurities (such as CN^- and Li^+) dissolved in alkali halides.⁵

The question of whether the tunneling dipoles at a very low impurity concentration c undergo a phase transition has not been answered until now. It is, however, expected that two effects will tend to inhibit the phase transition. These are (1) tunneling, which tends to disorient the dipoles, and (2) the random distribution of the dipole impurities at low concentrations c ($10^{-4} < c < 5 \times 10^{-2}$ in this work), which will introduce large fluctuations

in the random dipolar internal fields, thus reducing the tendency for a phase transition.

The purpose of this Letter is to examine the existence of a phase transition in the randomly distributed tunneling dipoles, using the mean-random-molecular-field (MRF) approximation.⁶ We show the following: (a) The dipoles undergo a new kind of phase transition, provided the average magnitude of the dipole fields $\eta_1(0)$ evaluated at temperature $T=0$ is greater than the tunneling matrix element δ . (b) In this transition, the average dipole moment (or polarization) for the system vanishes; however, the magnitude of the dipolar random order parameter m becomes non-zero below a well-defined transition temperature T_c . (c) The dielectric susceptibility χ is continuous; however, it has a discontinuous derivative (cusp) at T_c . (d) The behavior of χ near the transition temperature is given in terms of the moments of the probability of the distribution $f(E)$ of the random internal fields E . More specifically we find, for a specific case, that $T_c \propto c^\alpha$, where $\alpha \approx 0.66$ for $1\% < c < 5\%$. Finally, it is suggested that previous measurements^{7,8} of the susceptibility were performed in sufficiently large externally applied fields that they suppressed the cusp predicted by the present theory.

As the impurity concentration c goes to zero, we can neglect the interactions between the impurities. However, as c is increased, the dipole-dipole interactions between the impurities become important. The dipole Hamiltonian \mathcal{H}_D is

$$\mathcal{H}_D = \sum_{i,j} \frac{a}{r_{ij}^3 \epsilon_m} [\vec{\mu}_i \cdot \vec{\mu}_j - 3(\vec{\mu}_i \cdot \hat{r}_{ij})(\vec{\mu}_j \cdot \hat{r}_{ij})], \quad (1)$$

where r_{ij} is the distance between the dipoles $\vec{\mu}_i$ and $\vec{\mu}_j$ located at sites i and j , \hat{r}_{ij} is a unit vector in the direction of \vec{r}_{ij} , a is the strength of the dipole-dipole interaction including the effective field corrections, and ϵ_m is the dielectric constant of the host material.

The effect of the dipole-dipole interaction was studied theoretically by a number of investigators⁹ and experimentally by Kanzig, Hart, and Roberts⁷ and by Fiory.⁸ More recently Klein, Held, and Zuroff⁶ derived the probability distribution $f(E)$ of the dipolar internal fields E in the MRF approximation for the case when (1) the distance of closest approach of the dipoles is not limited by a near-neighbor interaction, but is allowed to approach zero, and (2) tunneling effects are completely neglected. This MRF approximation allows a self-consistent derivation of $f(E)$ from the Hamiltonian given in Eq. (1).

The derivations of the behavior of the six-orientational dipoles of KCl-OH^- near the transition region becomes somewhat involved algebraically. In order to simplify our presentation we show, instead, the derivation for a model in which the dipole is allowed to have two orientations only, with a tunneling matrix element δ connecting the up and down states, with a field E_T in the z direction, where $E_T = E_0 + E$, with E_0 the external and E the internal molecular field. Our step-by-step derivation for the two- and six-orientational dipoles is similar, except that the final result for the susceptibility χ near T_c will be given in terms of a simple function $\chi_1(T)$ which differs for the two cases, thus giving differing transition temperatures. At the end of our derivation, we give the result for the six-orientational case as well.

The energy levels for the two-orientational dipoles are obtained by diagonalizing a two-by-two matrix as in the work of Shore.⁴ We obtain for the two energy levels (letting $\mu = 1$) $\epsilon_{1,2} = \pm (E_T^2 + \delta^2)^{1/2}$. The partition function Z for a single dipole is $Z = 2 \cosh \beta (E_T^2 + \delta^2)^{1/2}$, and the polarization P is defined by $P = \partial \ln Z / \partial (\beta E_0)$. Thus

$$P(E_T, \beta) = \frac{E}{(E_T^2 + \delta^2)^{1/2}} \tanh \beta (\delta^2 + E^2)^{1/2}. \quad (2)$$

Because the positions of the dipoles are randomly distributed, the internal dipolar field is a random variable as was found in Ref. 6, where the probability distribution $f(\vec{E})$ of the random vector fields \vec{E} was derived. The work of Ref. 6 considers the case when tunneling effects are neglected and the distance of closest approach between the impurities is allowed to go to zero. We have rederived the results of Ref. 6 for the case when the distance of closest approach between the impurities is limited to a near-neighbor distance r_m and included tunneling effects. For the two-orientational dipoles the self-consistent probability distribution $f(E)$ for the z component (i.e., two-orientational) of the field E is

$$f(E) = (\pi b n_o m)^{-1} \int_0^\infty \cos x (E/bn_o m) \times \exp[-(4\pi/3)cx f(x)] dx, \quad (3a)$$

where $f(x) = \int_0^x [(1 - \cos t)/t^2] dt$, c is the impurity concentration, n_o is the number of sites per unit cell, $b = a/\epsilon_m$, and

$$m = \int_{-\infty}^\infty f(E) |P(E)| dE, \quad (3b)$$

with $P(E)$ given by Eq. (2) and the parallel bars indicating absolute values.

We remark that m given by Eq. (3b) appears as a parameter in Eq. (3a). Thus Eq. (3a) is an integral equation for the probability distribution of the field $f(E)$. We also note that E on the right-hand side of Eq. (3a) is divided by m ; thus the width of the probability distribution will be proportional to m . m enters naturally into our self-consistent solutions; however, it will become clear later on that the dipolar random order parameter m defined by Eq. (3b) is really an order parameter.

Examining Eq. (3a) for large and small fields, we have

$$\begin{aligned} f(E) &\approx \pi^{-1} \Delta_1 / (\Delta_1^2 + E^2), \quad E \ll bm, \\ f(E) &\approx (2\pi \Delta_2^2)^{1/2} \exp(-E^2/\Delta_2^2), \quad E \gg bm, \end{aligned} \quad (4)$$

where $\Delta_1 = \Delta_1(0)m$ and $\Delta_2 = \Delta_2(0)m$, where $\Delta_1(0) = 2\pi^2 a n_0 c / 3\epsilon_m$ and $\Delta_2(0) = (2\pi/3)^{1/2} a n_0 c^{1/2} / \epsilon_m$. The results of Eqs. (3) and (4) are similar to those obtained by Riess and Klein¹⁰ for the spin-glass problem.¹¹

For very high temperatures a solution to Eq. (3a) and (4) is $m = 0$; and since the width of the distribution is proportional to m , the width goes to zero as $m \rightarrow 0$ and $f(E) \rightarrow \delta(E)$, where $\delta(E)$ is the Dirac δ function.

In order to examine our equation for a possible phase transition we expand $P(E_T)$ in Eq. (2) in a power series in small E_T for high T [this is valid since for high T , $f(E) \approx \delta(E)$ and only very small fields contribute to the evaluation of m in Eq. (4)] and substitute the result into Eq. (4). Expanding Eq. (2) for small E_T gives

$$P = \chi_1(\beta) E_T - \chi_3(\beta) E_T^3, \quad (5)$$

where

$$\chi_1(\beta) = \tanh(\beta\delta) / \delta, \quad (6)$$

and $\chi_3 = (\tanh\beta\delta - \beta\delta \operatorname{sech}^2\beta\delta) / 2\delta^3$.

Let

$$\eta_n = \int_{-\infty}^{\infty} f(E) |E|^n dE, \quad (7)$$

where η_n is the n th moment of the distribution function $f(E)$. It directly follows from Eq. (3a) that

$$\eta_n = \eta_n(0) m^n, \quad (8)$$

where $\eta_n(0)$ is the n th moment of the distribution function evaluated at $T = 0$.

Substituting Eq. (5) into Eq. (4) and integrating gives for high T

$$m = \chi_1(\beta) \eta_1(0) m - \chi_3(\beta) \eta_3(0) m^3 + O(m^5). \quad (9)$$

Examining Eq. (9) we find that $m = 0$ for very high T and that m has a nonzero solution below the temperature $T_c = \beta_c^{-1}$ (with $k_B = 1$), $\chi_1(\beta) \eta_1(0) = 1$. Thus,

$$\chi_1(\beta_c) \eta_1(0) = 1 \quad (10a)$$

and

$$\tanh\beta_c \delta = \delta / \eta_1(0). \quad (10b)$$

For $\delta \geq \eta_1(0)$ there is no solution, whereas when $\delta \ll \eta_1(0)$ we have

$$T_c \approx \eta_1(0) \{1 - \frac{1}{3} [\delta / \eta_1(0)]^2\}. \quad (11)$$

The general solution to Eqs. (10) is

$$T_c = \frac{2\delta}{\ln[(1+x)/(1-x)]} \quad (12)$$

with $x = \delta / \eta_1(0)$.

Since $\eta_1(0)$ is the average magnitude of the internal field at $T = 0$; $\eta_1(0)$ will decrease as the impurity concentration decreases; and below a certain concentration c_0 there will be no phase transition. To get a feeling for the concentration dependence of $\eta_1(0)$, we note that $\eta_1(0)$ must be a function of the parameters Δ_1 and Δ_2 entering $f(E)$. Since for $E \gg am$, $f(E)$ is characterized by the width $\Delta_2(0) \propto c^{1/2}$ and for $E \ll am$, $f(E)$ is characterized by the width $\Delta_1(0) \propto c$, we expect $\eta_1(0) \propto c^\alpha$, with $0.5 < \alpha < 1$. We calculated $\eta_1(0)$ with a computer using the analytic expression for $f(E)$ given in Eq. (3a). We find that for the two-orientational dipoles and $\delta \ll \eta_1(0)$

$$\eta_1(0) \propto c^\alpha, \quad (13)$$

with $\alpha \approx 0.66$ for $1\% < c < 5\%$. Equation (13) is also the result obtained for spin-glasses.¹⁰

For T just below T_c we obtain from Eq. (9)

$$m(T) = \left(\frac{\chi_1(\beta) \eta_1(0) - 1}{\chi_3(\beta) \eta_1(0)} \right)^{1/2}, \quad T \lesssim T_c. \quad (14)$$

Substituting the value of $\chi_1(\beta)$ we find that for sufficiently large $\eta_1(0)$ [$\eta_1(0) > \delta$] $m(T)$ is proportional to $(T_c - T)^{1/2}$ near T_c . Thus m becomes nonzero below $T = T_c$. In our derivation, the local internal field experienced by a dipole is zero for $T > T_c$ and becomes nonzero for $T < T_c$. How does one measure the onset of order in an experiment? One method which comes to mind is an experiment analogous to the μ -meson depolarization performed by Murnick, Fiory, and Koesler.¹² The indirect result of the ordering upon the susceptibility χ is discussed below.

We next obtain the polarization and susceptibility of N_d dipoles. Since $f(E)$ is symmetric in E ,

we immediately obtain that $P(\beta)$ equals $\int f(E)P(E, \beta) dE = 0$ for all T , provided the external field is zero.

χ near T_c is obtained by differentiating $P(E, T, \beta)$ with respect to E_0 ; then letting $E_0 \rightarrow 0$, we have

$$\begin{aligned} \chi &= N_d \int f(E) [\chi_1(\beta) - 3\chi_3(\beta)E^2] dE \\ &= N_d [\chi_1(\beta) - 3\chi_3(\beta)\eta_2(0)m^2]. \end{aligned} \quad (15)$$

For $T > T_c$, $m = 0$, and Eq. (15) gives

$$\chi = N_d \chi_1(\beta), \quad T > T_c, \quad (16)$$

and

$$\begin{aligned} \chi &= N_d \left(\chi_1(\beta) + \frac{3\eta_2(0)}{\eta_3(0)} [1 - \chi_1(\beta)\eta_1(0)] \right), \\ T &\approx T_c. \end{aligned} \quad (17)$$

Using the fact that $1 - \chi_1(\beta)\eta_1(0) \propto T_c - T$ near T_c we obtain from Eq. (17) that χ is continuous at $T = T_c$, but there is a discontinuous derivative (cusp) in χ at $T = T_c$. For the case $\eta_1(0) \gg \delta$, we have that $\chi(T_c) \approx Nd/T_c \approx c^{1-\alpha} \approx c^{0.33}$ for $1\% < c < 5\%$.

So far we have considered the two-orientational dipoles. For OH^- in KCl (six orientations) Equations (16) and (17) still hold, except that ${}_2\chi_1 \rightarrow {}_6\chi_1$, where the subscript on the lower left indicates the number of orientations, and

$${}_6\chi_1(\beta) = \frac{1}{3\delta} \left(\frac{1 + 3e^{-2\beta\delta} - 4e^{-3\beta\delta}}{1 + 3e^{-2\beta\delta} + 2e^{-3\beta\delta}} \right) \quad (18)$$

with the single dipole tunneling energy being $\delta/2$. From Eqs. (18) and (10a) we obtain

$$T_c = \frac{3\delta}{\ln[(A+B)^{1/3} + (A-B)^{1/3}]},$$

where $A = (2+y)/(1-y)$, $B = \{1 + [(2+y)/(1-y)]^2\}^{1/2}$ and $y = 3\delta/\eta_1(0)$. For this case we have a nonzero transition temperature provided $\eta_1(0) > 3\delta$. For $\delta \ll \eta_1(0)$, we obtain $T_c = \eta_1(0)/3$ instead of $T_c = \eta_1(0)$ for the two-orientational case. The c dependence of the six-orientational $\eta_1(0)$ still remains to be calculated. However an examination of the results for the first moment of the distribution function for the vector field E derived in Ref. 6 shows that the value of $\eta_1(0)$ can only depend upon $\Delta_1(0)$ and $\Delta_2(0)$ given in Eq. (3). Thus an equation of the form given by Eq. (13) will still hold, with $0.5 < \alpha < 1$.

Kanzig, Hart, and Roberts⁷ and Fiory⁸ measured the low-temperature dielectric constant of dipole impurities in alkali halides and detected no cusps in the susceptibility. We suggest that the cusps were absent because the polarization was measured in relatively large applied fields

which suppressed the cusp in an analogous fashion to that observed in spin-glasses¹¹ when a large magnetic field is applied to the system. In order to observe the cusp E_0 would have to be very close to zero. By comparing the dipole system to the spin-glass system, we estimate that E_0 has to be of the order of 100 V/cm or less.

Finally we estimate the minimum concentration necessary to observe the cusps in OH^- in KCl. Using the maximum in the susceptibility observed by Kanzig, Hart, and Roberts⁷ the strength of the interaction can be obtained from Eq. (3-11) of Ref. 6. From this we estimate that the value of c necessary to observe the cusp is $c > 0.05\%$.

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¹V. Kuhn and F. Lütty, *Solid State Commun.* **2**, 281 (1964).

²M. E. Bauer and W. R. Saltzman, *Phys. Rev.* **178**, 1440 (1969).

³M. Gomez, S. P. Bowen, and J. A. Krumhansl, *Phys. Rev.* **153**, 1009 (1967).

⁴H. B. Shore, *Phys. Rev.* **151**, 570 (1966).

⁵V. Narayanamurty and R. O. Pohl, *Rev. Mod. Phys.* **42**, 201 (1970); W. E. Bron and R. W. Dreyfus, *Phys. Rev.* **163**, 304 (1967); G. Feher, I. W. Shepherd, and H. B. Shore, *Phys. Rev. Lett.* **16**, 500, 1187 (1966); F. Lütty, *Phys. Rev. B* **10**, 3667 (1974); S. Kapphan and F. Lütty, *J. Phys. Chem. Solids* **34**, 969 (1973), and *Phys. Rev. B* **6**, 1537 (1972); P. P. Perissini, J. P. Harrison, and R. O. Pohl, *Phys. Rev.* **182**, 939 (1969).

⁶M. W. Klein, C. Held, and E. Zuroff, *Phys. Rev. B* **13**, 3576 (1976).

⁷W. Kanzig, H. R. Hart, and S. Roberts, *Phys. Rev. Lett.* **13**, 543 (1964).

⁸A. T. Fiory, *Phys. Rev. B* **4**, 614 (1971).

⁹R. Brout, *Phys. Rev. Lett.* **14**, 176 (1965); W. Zernik, *Phys. Rev.* **139**, A1010 (1965); M. W. Klein, *Phys. Rev.* **141**, 489 (1966); W. N. Lawless, *Phys. Kondens. Mater.* **5**, 100 (1966); W. N. Lawless, *J. Phys. Chem. Solids* **30**, 1161 (1969).

¹⁰I. Riess and M. W. Klein, to be published.

¹¹J. A. Mydosh, in *Magnetism and Magnetic Materials—1974*, AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., J. J. Rhyne, and G. H. Lander (American Institute of Physics, New York, 1975), p. 131; V. Conella and J. A. Mydosh, *Phys. Rev. B* **6**, 4220 (1972).

¹²D. E. Murnick, A. T. Fiory, and W. J. Koessler, *Phys. Rev. Lett.* **36**, 100 (1976).