Elastic Softening and Ferroelastic Instabilities in Alkali Cyanides and Superoxides

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(Received 9 November 1981)

It is shown that the competition between short-range repulsion and the interaction between quadrupole moment and fluctuating field gradient strongly influences the elastic softening and ferroelastic instabilities of ionic molecular solids. This theory is applied to explain the ferroelastic properties of alkali cyanides and superoxides.

PACS numbers: 63.75.+z, 64.70.Kb

One of the most interesting properties of molecular crystals is that they undergo ferroelastic phase transitions (FEPT) accompanied by orientational melting. In the high-T phase the crystals show unusual thermoelastic behavior. With decreasing T, the elastic constants C_{11} and C_{44} show anomalous softening and the crystals undergo FEPT to a structure of lower symmetry. Typical examples are alkali cyanides (MCN) and alkali superoxides (MO_2); these systems have been extensively studied in recent years.[1-6]

In this Letter we show how the nature of elastic softening and the ferroelastic instability depend sensitively on the competition between short-range repulsive forces and the interaction between quadrupole moment Q of the molecular ions (CN^- and O_2^-) and the fluctuating electric-field gradient (efg) present in the high-T cubic phase. Our theory explains the qualitative differences between cyanides and superoxides and the dependence of the FEPT temperature on the lattice constant for different cyanides.

The anomalous elastic softening[1] in KCN was discussed in terms of translational-rotational (TR) coupling by Michel and Naudts,[4] who considered only short-range repulsion effects to explain the experiment[1] ($C_{44} \to 0$ at a temperature T_{44} which is higher than T_{11} at which $C_{11} \to 0$). Within such an approximation it is difficult to see how an equivalent system, namely KO_2, would show the opposite behavior[7] ($T_{11} > T_{44}$). It is known[8] that the coupling between Q and the efg is important in the stability of noncubic structures. Furthermore, a recent molecular-dynamics study[5] of the rotational autocorrelation function in the cubic phase of KCN has shown the importance of including anisotropic electrostatic forces for a proper understanding of the experimental probability distribution functions. We have therefore studied the effect of the interaction between Q and the fluctuating efg (present in the cubic phase) on the rotational-translational coupling and find that this plays a significant role in the microscopic understanding of ferroelastic properties of these solids.

Elastic properties of ionic molecular solids can be studied by considering a TR Hamiltonian $H = H_T + H_R + H_{TR}$, where

$$H_T = \sum_{j\vec{k}} \hbar\omega_{j\vec{k}}^0 (b_{j\vec{k}}^\dagger b_{j\vec{k}} + \tfrac{1}{2}), \tag{1}$$

$$H_R = \tfrac{1}{2} \sum_{k\alpha\beta} Y_\alpha^\dagger(\vec{k}) D_{\alpha\beta}(\vec{k}) Y_\beta(\vec{k}) + \sum_{i=1}^{N} V(\hat{n}_i), \tag{2}$$

$$H_{TR} = i \sum_{k\alpha j} Y_\alpha^\dagger(\vec{k}) V_{\alpha j}(\vec{k}) (b_{j\vec{k}} + b_{j-\vec{k}}^\dagger). \tag{3}$$

$\omega_{j\vec{k}}^0$ is the frequency of a bare phonon of wave vector $\vec{k}$ and polarization j described by the creation ($b_{j\vec{k}}^\dagger$) and destruction ($b_{j\vec{k}}$) operators. $V(\hat{n}_i)$ is the single-site cubic potential when centers of mass are fixed at the fcc lattice sites. The orientational order parameters $Y_\alpha(\vec{k})$ are the lattice Fourier transforms of $Y_\alpha(\hat{n}_i)$'s which are symmetrized (e_g and t_{2g}) combinations of spherical harmonics of order 2; $\hat{n}_i$ is the orientation vector of the molecule at $\vec{R}_i$.

The coupling between the orientational order parameter $Y_\alpha(\vec{k})$ and the phonon $\vec{k}j$ is given by $V_{\alpha j}(\vec{k})$. In the earlier theoretical work,[4] only the repulsion (between CN^- and M^+) contribution to $V_{\alpha j}(\vec{k})$ was considered. However, as the lattice vibrates there is deviation from local cubic symmetry at the positions of the molecules and the resulting efg couples to Q. This coupling contributes to $V_{\alpha j}(\vec{k})$ and depending on the sign of Q it will either enhance or suppress the TR coupling in these systems.

Before discussing these two contributions to $V_{\alpha j}(\vec{k})$, let us look at the effect of H_{TR} on the bare elastic constants C_{11}^0 and C_{44}^0. The renormalized phonon frequencies are given by[9]

$$\omega_{j\vec{k}}^2 = (\omega_{j\vec{k}}^0)^2 - 2\omega_{j\vec{k}}^0 \sum_{\alpha\beta} V_{\alpha j}(\vec{k}) \chi_{\alpha\beta}(\vec{k}) V_{\beta j}^*(\vec{k}), \tag{4}$$

where $\chi_{\alpha\beta}(\vec{k})$ is the isothermal rotational susceptibility obtained in the presence of direct interaction $D_{\alpha\beta}(\vec{k})$. $V_{\alpha j}(\vec{k})$ is given by

$$V_{\alpha j}(\vec{k}) = (2\omega_{jk}^{0})^{-1/2} \sum_{\mu=x,y,z} [\epsilon_\mu(+|\vec{k}j)v_{\alpha\mu}^{+}(\vec{k}) + \epsilon_\mu(-|\vec{k}j)v_{\alpha\mu}^{-}(\vec{k})], \tag{5}$$

where $v_{\alpha\mu}^{\pm}(\vec{k})$'s are the couplings between $Y_\alpha^{\dagger}(\vec{k})$ and the Fourier transforms $u_\mu^{\pm}(\vec{k})$ of the positive- and negative-ion displacements; $\epsilon_\mu(\pm|\vec{k}j)$ are the corresponding polarization vectors of a given mode $\vec{k}j$. Only the short-range repulsion contributes significantly to $v_{\alpha\mu}^{+}(\vec{k})$ whereas the fluctuating efg contributes to both $v_{\alpha\mu}^{+}$ and $v_{\alpha\mu}^{-}$, although there are important cancellation effects.

To calculate C_{11} and C_{44} we consider the LA and TA phonons with $\vec{k}=(0,0,k)$ in the limit $k\rightarrow 0$. For $(0,0,k)$ phonons, we have $\omega_{\mathrm{LA}}^2=(C_{11}/\rho)k^2$ and $\omega_{\mathrm{TA}}^2=(C_{44}/\rho)k^2$ where ρ is the mass density. For symmetry reasons, in Eq. (4), ω_{LA} couples to χ_{11} (e_g susceptibility) and ω_{TA} couples to χ_{44} (t_{2g} susceptibility). The renormalized elastic constants are given (in the notation of Ref. 4) by

$$C_{11}=C_{11}^{0}-(8/a)(A_R+A_Q)^2\chi_{11}(T), \tag{6a}$$

$$C_{44}=C_{44}^{0}-(2/a)(B_R+B_Q)^2\chi_{44}(T), \tag{6b}$$

where a is the nearest-neighbor distance and

$$A_Q=(9\pi/5)^{1/2}Q|e|/a^4=-(3/2)^{1/2}B_Q. \tag{7}$$

In Eqs. (6a) and (6b) A_R and B_R are the repulsion contributions which are complicated functions of repulsion parameters[4] whereas A_Q and B_Q are quadrupole contributions. Typically, $B_R/A_R \cong -0.25$ whereas $B_Q/A_Q=-0.82$. This suggests that the nature of C_{11} and C_{44} softening is different for these two different coupling mechanisms.

In considering the contributions to A_Q and B_Q from different neighbors we find that there is a nearly perfect cancellation between second and third neighbors, the fourth one making only a few percent contribution. Thus to the leading order only the nearest-neighbor positive ion contributes to the fluctuating efg.

For KCN, using Tosi-Fumi parameters[5] for CN^- and K^+ repulsion, we find that $A_R=4379$ K/Å and $B_R=-988$ K/Å. Taking the free-ion value[5] of Q for the CN^- ion, i.e., $Q=Q_0=-4.64\times10^{-10}$ esu Å^2, we find that $A_Q=-3440$ K/Å and $B_Q=+2808$ K/Å. For this sign of Q_0, A_Q and B_Q have opposite signs from those of A_R and B_R. Furthermore, B_Q is a factor of 3 larger than B_R and completely dominates the C_{44} softening [see Eq. (6b)]. On the other hand, A_Q and A_R are comparable in magnitude, the former being a factor of 1.3 larger. This calculation clearly indicates the importance of the mechanism that we have proposed. In particular, for systems with large negative Q, C_{44} instability is considerably enhanced because $\chi_{44}\gg\chi_{11}$ at the temperatures of physical interest.

We have calculated C_{11} and C_{44} as a function of T when $Q=0$. For bare elastic constants C_{11}^0 and C_{44}^0 we choose values appropriate for KCl at room temperature. The value of C_{44}^0 for KCN may be smaller because of differences in the negative-ion polarizabilities, but the choice made in Ref. 4 is too small. We find that in the limit $A_Q=B_Q=0$, C_{11} softens to zero at a higher temperature than C_{44}, i.e., $T_{11}/T_{44}=3.5>1$. This is still true if we reduce the strength of the repulsion by a factor of 2 which is quite unphysical. We conclude[10] that the repulsive forces influence C_{11} more strongly than C_{44} and since C_{11} couples to the order parameter Y_1, one expects a ferroelastic ordering of the molecules along the c axis when $C_{11}\rightarrow 0$. This is precisely the ordering seen[3] in the superoxides $\mathrm{KO_2}$, $\mathrm{RbO_2}$, and $\mathrm{CsO_2}$. If on the other hand we choose $A_R=B_R=0$, then $T_{11}/T_{44}=0.36<1$; the system shows a behavior similar to that seen in cyanides.[1] However, for a realistic description of the elastic behavior, A_R, A_Q, B_R, and B_Q should be considered.

To calculate C_{11} and C_{44} for the cyanides and superoxides we need to know the value of Q in the solid. Bounds, Klein, and McDonald,[5] in their molecular dynamics (MD) study of KCN, found that they had to reduce Q_0 by a factor $f=0.5$ to fit the experimental orientational probability distribution and argued that this reduction could be caused by charge rearrangement of CN^- molecules in the solid. In this MD study, volume fluctuations were not considered and therefore in the absence of an exact knowledge of f, we have chosen a slightly different value ($f=0.6$) to fit the experimental elastic constants (not an optimum fit). With this reduction factor, we are able to explain the results for NaCN, KCN, and RbCN fairly well.[9] For $\mathrm{O_2}^-$ we choose[8] $Q=-1.756$ esu Å^2.

For lack of space we show our results of the T dependence of C_{11} and C_{44} for KCN only. C_{11}^0 and C_{44}^0 were chosen to fit the experimental data at 453 K. Our results along with experimental data are given in Figs. 1 and 2. We also show the

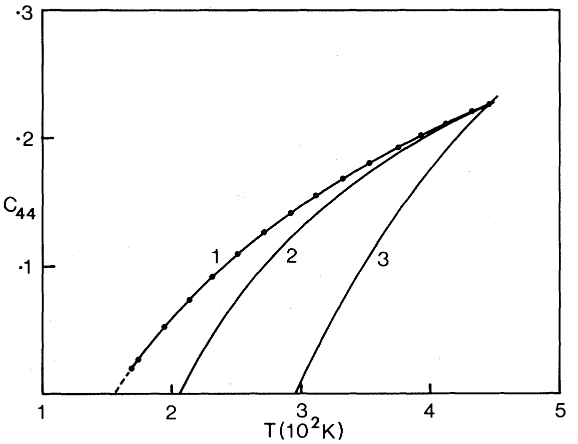

FIG. 1. Elastic constant C_{44} for KCN (in units of 10^{11} dyn/cm^2) as a function of temperature T with $C_{44}^0 = 0.41$. Curve 1, experiment (Ref. 1); curve 2, theory with $Q = 0.6Q_0$; and curve 3, theory with $Q = 0.75Q_0$.

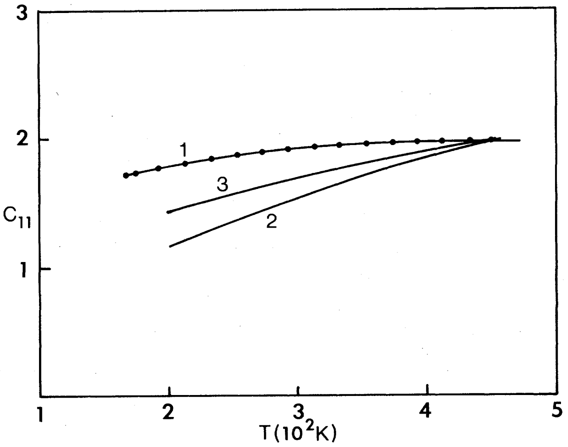

FIG. 2. Elastic constant C_{11} for KCN (in units of 10^{11} dyn/cm^2) as a function of temperature T with $C_{11}^0 = 3.9$. Curve 1, experiment (Ref. 1); curve 2, theory with $Q = 0.6Q_0$; and curve 3, theory with $Q = 0.74Q_0$.

results when $Q=0.75Q_0$. Clearly $Q=0.6Q_0$ gives a good fit to the data if we note that our theory for phonon renormalization and $\chi_{\alpha\beta}$ is of mean-field nature and neglects anharmonicity effects. Two points are worth noting: (i) A_R (=4379 K/Å) and A_Q (= −2064 K/Å) tend to cancel each other and a nonzero A_Q suppresses C_{11} softening; and (ii) since $D_{11}(\vec{k}=0) = -704$ K and $D_{44}(\vec{k}=0) = 235$ K, the direct quadrupole-quadrupole interaction tends to enhance C_{11} softening and suppress C_{44} softening, although the effect is ~10%.[11] Similar cancellation and direct-interaction effects are present[9] in NaCN and RbCN. The theoretical (experimental[12]) FEPT temperatures (in kelvins) are 340 (255.4), 210 (156), and 193 (130) for NaCN, KCN, and RbCN, respectively. The agreement appears to be fairly good if we note the mean-field nature of the present theory.

For superoxides, the elastic constants have not been measured extensively, but KO_2, RbO_2, and CsO_2 show an ordering of the type $\langle Y_1\rangle \neq 0$. Since Q_0 for O_2^- is a factor of 2.5 smaller than that for CN^- and since the repulsive forces are comparable,[9] C_{11} goes to zero at a higher temperature than C_{44}, thus explaining the $\langle Y_1\rangle \neq 0$ ordering in these three systems. For a quantitative understanding of T_c, one has to include the effect of orbital degeneracy of the O_2^- ion. In the case of NaO_2, because of dominating direct intermolecular interaction, an antiferroelastic ordering[8,13] takes place before the ferroelastic instability.

In conclusion we believe that the competition between repulsive and anisotropic interactions plays a very significant role in understanding the ferroelastic properties of alkali cyanides and superoxides and in ionic molecular solids in general.

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[7] Although C_{11} and C_{44} have not been measured in KO_2, RbO_2, and CsO_2, the observed (Ref. 3) CaC_2 structure $(\langle Y_1\rangle \equiv \langle Y_{20}\rangle \neq 0)$ in the ferroelastic phase suggests that $C_{11} \to 0$ at a higher temperature than C_{44}.

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[9] We replace $\chi_{\alpha\beta}(\vec{q}, \omega)$ by its $\omega \to 0$ limit which is adequate for studying the elastic behavior. Details of the calculation for cyanides and superoxides will be published in a larger paper.

[10] In Ref. 4, B_R was incorrectly given to be positive. Also there was a factor-of-2 error in the calculation of single-site susceptibilities which resulted in $T_{44}/T_{11} > 1$ (see text). For the values of repulsive parameters used in Ref. 4 we find that $T_{11} > T_{44}$ which is consistent with the findings of this paper.

[11] In the presence of direct interaction, $\chi_{ii}(\vec{k}=0)$

$= \chi_{ii}^0/[1 + D_{11}(\vec{k}=0)\chi_{ii}^0]$; in the present case $\chi_{44}/\chi_{44}^0 < 1$ and $\chi_{11}/\chi_{11}^0 > 1$.

[12] Since the ferroelastic phase transition is weakly first order, the transition temperature $T_c > T^* = T_{44}$, the temperature at which C_{44} extrapolates to zero. $T_c = 283.5$, 168, and 133 K for NaCN, KCN, and RbCN, respectively [see Y. Kondo *et al.*, Phys. Rev. B 19, 4210 (1979) for T_c].

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Rayleigh Linewidth Measurements on Binary Liquid Films near the Critical Point

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(Received 25 January 1982)

The first measurements are reported of the Rayleigh linewidth of binary liquid films near the critical point for which the correlation length is comparable to the film thickness. The present data are in good agreement with the predictions of renormalization-group theory for binary liquids in three spatial dimensions with no adjustable fitting parameters. No influence of finite size or bounding surfaces on the linewidth is observed.

PACS numbers: 64.60.Ht, 64.60.Fr, 64.70.Ja, 68.15.+e

For bulk binary liquid systems, measurements of the Rayleigh linewidth near the critical point are in excellent agreement with the predictions of dynamic renormalization-group (RG) theory. It is fair to say that the critical dynamics of these systems are well understood. The dynamical theory is not well understood, however, when bounding surfaces and the finite spatial extent of the system become relevant. Further, no experiments have been reported that investigate dynamical finite-size effects in binary liquid mixtures.

Consider films formed by placing a small amount of a binary liquid mixture at the bulk critical composition between two closely spaced optical flats. Such films can be made thin enough that the correlation length of order parameter fluctuations, ξ, becomes comparable to the film thickness, s, as the critical temperature is approached. It is in the regime $\xi \approx s$ that we expect the influence of finite size to become important.

It is difficult to know *a priori* the dynamic critical properties of such a film, the major problem being the correct determination of the dynamic universality class for this system. As a first guess, we might expect the class to be that of a three-dimensional (3D) binary liquid when $\xi < s$, and cross over to that of a two-dimensional (2D) liquid when $\xi > s$. There is some experimental evidence for this in the static critical behavior of liquid films.[1] However, the appropriateness of the equations governing the behavior in 2D is much less certain in the dynamic case than in the static case. For instance, the correct interpretation of the viscosity in 2D is uncertain.[2] In addition, recent work by Hurd, Mockler, and O'Sullivan[3] on particle diffusion in thin liquid films has shown that the zero-flow-velocity boundary condition at the surface of the optical flats cannot be ignored when the particle diameter becomes comparable to the film thickness. We expect that this boundary condition should be included in the fluid equations that govern the binary liquid films when ξ becomes comparable to s. We are unable to say how this would influence the behavior of the Rayleigh linewidth. We also might worry about the formation of surface layers on the optical flats. Recent theoretical[4] and experimental[5] work argues for the existence of a surface layer due to the preferential wetting of one liquid component on a solid surface. The thickness of this wetting layer may not be small compared to the film thickness. If it were of significant thickness, the film would neither be homogeneous nor at the critical composition. We would expect to measure a Rayleigh linewidth larger than that predicted by RG theory. However, it is not clear that the results of Refs. 4 and 5, which treat a solid surface in contact with a semi-infinite binary liquid, are relevant to our system in which the liquid film is isolated from the bulk liquid reservoir.

For the sake of argument, let us assume that surface layers are negligible and the correct dynamic universality classes are the 3D liquid class for $\xi < s$ and the 2D liquid class for $\xi > s$. We still must calculate the Rayleigh linewidth as a function of temperature in 2D. The only scheme that we know of is the ϵ expansion,[6] which is a poor approximation in 2D. The agreement be-

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