Theory of the Orientational Glass State in $M(\mathrm{CN})_x X_{1-x}$ Mixed Crystals

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A microscopic model of mixed crystals with orientational disorder and translation-rotation coupling is proposed. The substitutional halogens generate random strain fields which couple to the orientational modes. At large fields, the ferroelastic phase transition is suppressed. The anomalous behavior of acoustic phonons is studied. The central peak is obtained as a static phenomenon. Qualitative agreement with a number of experimental results is obtained.

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Below a concentration x_c of CN^-, mixed crystals $M(\mathrm{CN})_x X_{1-x}$, where M is an alkali metal and X a halogen ion, no longer display a ferroelastic phase transition to a low-symmetry state with long-range order.[1] The transverse acoustic phonon frequency exhibits a rounded minimum at a temperature $T = T_f(x)$.[2–4] Below T_f, a sharp central peak, the intensity of which grows strongly with decreasing T, is found by neutron scattering.[2,5,6] The average lattice structure stays cubic[1,7] for $x < x_c$. These experimental facts suggest that for $T < T_f$, the system freezes into an orientational glass state.[5] The bilinear translation-rotation (T-R) coupling leads to a simultaneous freezing in of translational and orientational modes of T_{2g} symmetry.[8] Theoretical work has been based on the assumption of randomness of the quadrupolar interaction.[9] At $T_d < T_f$, there is ample experimental evidence for dipolar freezing.[10,11] So far there exists no coherent explanation of the experimental facts.

From the experimental observation[1,4] that $x_c \approx 0.2$ for $M = \mathrm{K}$ and $X = \mathrm{Cl}$ and that $x_c \approx 0.4$ for $M = \mathrm{K}$ and $X = \mathrm{Br}$, I conclude that the substitutional halogens play an important role. Using the theory of defects in solids,[12] I calculate the change of forces $\Delta \mathbf{F}^X$ which are exerted on the surrounding crystal by the substitutional halogens. These forces lead to static, temperature-independent strain fields h_α which couple to the orientational degrees of freedom Y_α of the CN^- ions:

$$V^{SR} = \sum_k Y_\alpha(\mathbf{k})\, h_\alpha(-k, \{\sigma\}), \tag{1}$$

$$h_\alpha(-\mathbf{k}, \{\sigma\}) = \sum_{\mathbf{n}} \{(1-x) - [1-\sigma(\mathbf{n})]\}\, v_{\alpha i}(\mathbf{k}) A_i(\mathbf{k}) \exp[i\mathbf{k}\cdot\mathbf{X}(\mathbf{n})]. \tag{2}$$

Here $\{\sigma\}$ denotes a quenched configuration of CN^- ions, with $\sigma(\mathbf{n}) = 1$ or 0, depending on the presence of CN^- or X^-, respectively, at site $\mathbf{n}$. The matrix $v_{\alpha i}(\mathbf{k})$ represents the bilinear T-R coupling.[13] The index α labels the three modes with $l = 2$ and T_{2g} symmetry.[13] $\mathbf{A}(\mathbf{k}) = M^{-1}(k)\mathbf{v}^X(\mathbf{k})$ is the amplitude of lattice strains.[12] Here $M(\mathbf{k})$ is the acoustic bare dynamical matrix and $\mathbf{v}^X \propto \Delta \mathbf{F}^X$. Denoting the configurational average by an overbar, and using the fact that the distribution of halogens is random, we have

$$\overline{h_\alpha(\mathbf{n})} = 0, \quad \overline{h_\alpha^2(\mathbf{n})} = x(1-x)h^2, \tag{3}$$

where $h^2 = (1/N)\sum_{\mathbf{k}}[v_{\alpha i}(\mathbf{k})A_i(\mathbf{k})]^2$. Properties (3) are characteristic for random-field systems.[14]

In addition to the static strain coupling (1), I have the interaction of orientational modes with dynamic acoustic lattice vibrations $s_i(\mathbf{k})$,[13]

$$V^{TR} = \sum_k Y_\alpha(\mathbf{k}) v_{\alpha i}(\mathbf{k}) s_i(\mathbf{k}). \tag{4}$$

I also include the usual elastic interaction V^{TT} with dynamical matrix $M(\mathbf{k})$, the direct rotational interaction V^{RR} with coupling $J(\mathbf{k})$, and an orientational crystal-field potential V^R. Using these potentials, I calculate the free energy F for a configuration $\{\sigma\}$. The term V^{SR} plays the role of an external random field.[14] Finally, I take the configurational average by using Eqs. (3). Up to second order, I find within molecular-field theory

$$\bar{F} = \bar{F}_R + \tfrac{1}{2}\sum_k \{\mathbf{s}^{e\dagger}(\mathbf{k}) M(\mathbf{k}) \mathbf{s}^e(\mathbf{k}) + 2\mathbf{Y}^{e\dagger}(\mathbf{k}) v(\mathbf{k}) \mathbf{s}^e(\mathbf{k}) + [(\chi^0)^{-1} + J(\mathbf{k}) + C^s]\mathbf{Y}^{e\dagger}(\mathbf{k})\mathbf{Y}^e(\mathbf{k})\}. \tag{5}$$

Here $\bar{F}_R$ is the crystal-field contribution, $\mathbf{s}^e$ and $\mathbf{Y}^e$ are the instantaneous values of the translational coordinates, C^s is the orientational self-energy, and χ^0 the local susceptibility

$$\chi^0 = x(y/T)[1 - x(1-x)\xi h^2/T^2]. \tag{6}$$

The functions y and ξ are weakly temperature dependent. If one takes $\mathbf{k} = (0,0,k)$, all matrices become diagonal. The collective orientational susceptibility is obtained from Eq. (5) as

$$\chi^{YY} = \chi^0/(1-\delta\chi^0), \tag{7}$$

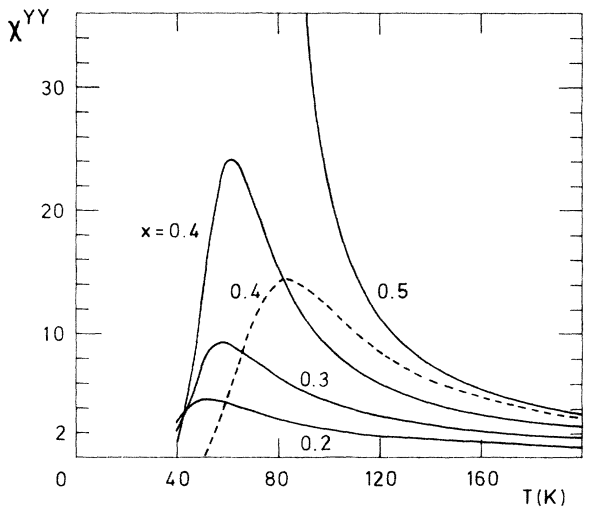

FIG. 1. Collective orientational susceptibility χ^{YY} as a function of temperature; $h=300$ K for continuous curves, $h=400$ for broken curve. CN concentration x as indicated.

where δ is the largest eigenvalue of the total orientational interaction $[v^{\dagger}M^{-1}v-J-C^{s}]$. If $h=0$, χ^{YY} diverges at a temperature $T_c=xy\delta$, which reflects a second-order phase transition. If $h\neq 0$ and is sufficiently large, χ^{YY} stays finite and shows a rounded maximum, as is shown in Fig. 1. Numerical calculations yield $h=150$ K for the bromine and 450 K for the chlorine mixed crystal. One should not overemphasize the absolute value of these numbers since the microscopic interaction potentials are loaded with some uncertainties.[15]

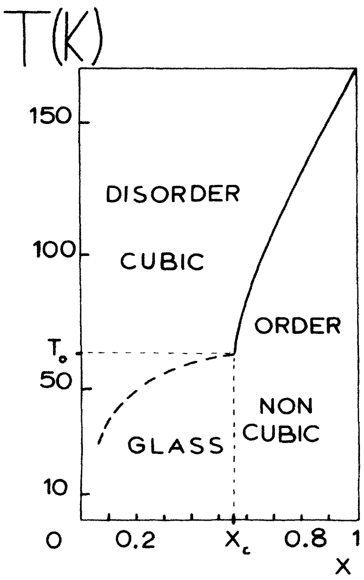

FIG. 2. Phase diagram for $K(CN)_xBr_{1-x}$ as a function of concentration and temperature, with values $\xi=0.06$, $h=294$ K chosen as parameters. To be compared with Fig. 1 of Ref. 7.

On the basis of the expressions (5) and (6) I have calculated the phase diagram as a function of concentration x and temperature. The result is shown in Fig. 2. There x_c is the lowest value of x where the ferroelastic transition to an ordered state occurs; T_0 is the corresponding temperature. The orientational glass state occurs for $x<x_c$ and $T_f(x)<T$.

The transverse-acoustic phonon frequencies $\omega^2(k)$ are given by $D_{11}(k)$, the inverse of the displacements susceptibility $\langle s^{\dagger}(k)s(k)\rangle/T$. I obtain

$$D_{11}(k)/M_{11}(k)=\left(\frac{1-\chi^0\delta}{1+(J+C^s)\chi^0}\right), \tag{8}$$

which is equal to the ratio of elastic constants c_{44}/c_{44}^0. The T and x dependence is shown in Fig. 3; it agrees with experiment.[3]

The position of the minimum T_f depends on the frequency of the experimental method.[5,16] I therefore consider the dynamic correlation function

$$S_{11}^{ss}(k,\omega)=\frac{T\Delta_{11}f(\omega)}{[\omega^2-D_{11}(k,\omega)]^2+[\omega\Delta_{11}f(\omega)]^2}, \tag{9}$$

where

$$D_{11}(k,\omega)=D_{11}(k)+\omega^2\Delta_{11}f(\omega)/\lambda, \tag{10}$$

with $f(\omega)=\lambda/(\omega^2+\lambda^2)$. Here $\Delta_{11}(k)=M_{11}(k)-D_{11}(k)$, and λ accounts for orientational relaxation. I take $\lambda(T)=\lambda_0(T/240)^{1/2}$ with $\hbar\lambda_0=1$ THz. The temperature behavior of $D_{11}(k,\omega)$ and of the damping $\Gamma(k,\omega)=\omega\Delta_{11}f(\omega)$ is shown in Fig. 4. Here the qualitative agreement with experiments[16,17] is also very good.

The static strain interaction V^{SR} leads to the appearance of a central peak. Since locally, the cubic symmetry is broken,[8] I obtain at lattice site l

$$\langle Y_\alpha(l)\rangle=-(y/T)h_\alpha(l,\{\sigma\}). \tag{11}$$

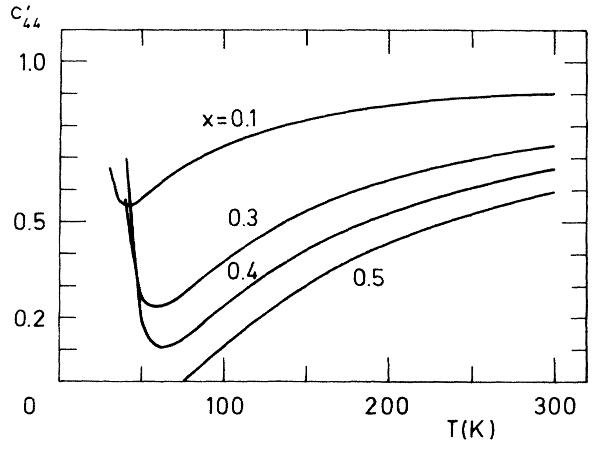

FIG. 3. Temperature dependence of elastic constants $c_{44}'\equiv c_{44}/c_{44}^0$ for $h=300$ K and CN concentration $x=0.1$, 0.3, 0.4, and 0.5.

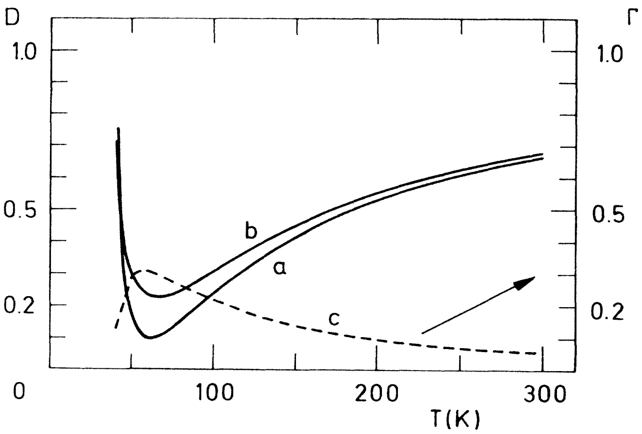

FIG. 4. Temperature dependence of $D \equiv D_{11}(k,\omega)/M_{11}(k)$ for (curve *b*) $\omega = 0.2$ THz, (curve *a*) $\omega = 0.0$. Broken curve shows damping $\Gamma \equiv \Gamma(\omega)/M_{11}(k)$, $\omega = 0.2$ THz. In all cases $x = 0.4$ and $h = 300$ K.

Relations (3) imply that $\langle \overline{Y} \rangle = 0$ and

$$\overline{\langle Y_\alpha(1) \rangle^2} = x\Psi, \tag{12}$$

where $\Psi = (y/T)^2 h^2 x(1-x)$ is the orientational glass-state order parameter. As a result of T-R coupling, it can be seen that $\overline{s_l(\mathbf{n})} = 0$, but $\overline{\langle s_l(\mathbf{n}) \rangle^2} \propto x\Psi$. The property (12) leads to the existence of a static central peak in addition to the dynamic part of the scattering law.[8] A similar separation of a static part (due to a breaking of local symmetry) and a dynamic part (due to time-dependent fluctuations) was previously made for the description of displacement fields in the presence of frozen interstitial defects.[18] The asymmetric shape of the intensity contours in **Q** space[5] of the central peak *is* a direct signature of T-R coupling of T_{2g} symmetry.[8] Deviations from cubic symmetry on a local scale in the lattice are reflected in the temperature dependence of x-ray diffraction linewidths[7] and in a temperature-dependence distribution of electric-field gradients as measured by NMR.[19] I conclude, therefore, that these phenomena must be proportional to Ψ and have the same temperature dependence as the intensity of the central peak. My calculations of $\overline{F}$ have been based on classical statistical mechanics; therefore my results break down at low $T \lesssim 30$ K where a quantum-mechanical treatment is required.[20] However, the physical mechanism, which is based on the coupling of random strain fields to orientational modes, is still valid. I also expect that my theory can be extended to a description of strain coupling to orientational modes of T_{1u} symmetry. Such an extension should be relevant for a description of the dipolar glass state.[10,11]

Previously it has been remarked[13] that the lattice-mediated interaction in KCN bears analogies to the system of hydrogen dissolved in pure metals. Recently it has been shown that hydrogen dissolved in metallic alloys can be considered as a lattice gas with internal random fields.[21] This point of view is analogous to the one I have adopted here for the description of mixed crystals with orientational disorder. A detailed account of the present work will be given elsewhere.

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