

served fact that the spectrum obtained with HD is simply the superposition of the spectra measured with H₂ and D₂ is, therefore, not the result of an accidental degeneracy. The very important conclusion to be drawn is that the molecular models are not valid and that the β_1 and β_2 phases of hydrogen on W(001) are of atomic nature.

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Anomalous Thermoelastic Behavior and Molecular Reorientations in Crystals

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We have derived a microscopic Hamiltonian that takes into account rotational-translational coupling in molecular crystals. This coupling leads to an effective orientational interaction among nonspherical molecules. It is responsible for an anomalous behavior of the elastic constants and of the transverse-acoustic phonons. The temperature behavior of c_{44} and c_{11} in KCN above the 168-K phase transition is explained.

In molecular liquids it is well established that there exists a dynamical coupling between translational and orientational modes.^{1,2} More recently, the importance of a static coupling between translation and rotation has been realized for molecular crystals and used to explain Rayleigh-Brillouin measurements.³ This coupling should also be responsible for the drastic thermoelastic anomalies (softening of elastic constants⁴) that have been found near some orientational phase transitions in molecular crystals. This effect was discovered by ultrasonic methods⁴ and confirmed by Brillouin scattering.⁵ It manifests itself also very clearly in recent neutron scattering experiments⁶ where one finds a softening of transverse-acoustic phonons. To our knowledge, there exists no microscopic theory that describes in a satisfactory way the static coupling between

translation and reorientation in solids. Also, the experiments⁴⁻⁶ have found so far no theoretical explanation. The purpose of this Letter is twofold: First, we want to derive from a realistic microscopic-force model a Hamiltonian that contains such a static coupling. Second, we will apply this Hamiltonian to explain the experiments⁴⁻⁶ and to clarify the situation near the orientational phase transition.

To be specific, our theory will be most closely related to $M(XY)$ compounds, say KCN, but its generalization to other substances will be obvious. In the high-temperature phase ($T > T_c = 168$ K), KCN has a cubic structure where the linear (CN)⁻ ions are surrounded by an octahedral cage of the K⁺ ions. The (CN)⁻ ions assume octahedral symmetry by reorienting among equivalent orientations.⁷ At T_c , there is a phase

transition to an orthorhombic structure in which the $(\text{CN})^-$ ions are oriented along the b axis. The sense of the $(\text{CN})^-$ ions is not fixed at this transition.

We consider now the following model to describe the cubic phase of $M(\text{XY})$ compounds. Since the sense of the $(\text{XY})^-$ ions is not relevant here, we replace the linear $(\text{XY})^-$ ions by a dumbbell molecule of length $2d$. Each dumbbell is surrounded by six M atoms in octahedral positions at equilibrium distance a . The two ends of the dumbbell act as repulsive centers with respect to the M atoms. The interaction is described by the well-known Born-Mayer repulsive overlap potential⁸ summed over the two ends ($s = \pm 1$) of the dumbbell:

$$V_{ni}^{OT} = C_1 \sum_{s=\pm 1} \exp(-C_2 |\vec{R}_n^- + s\vec{d} - \vec{R}_i^+|). \quad (1)$$

Here, R_n^- and R_i^+ denote, respectively, the center-of-mass positions of the n th dumbbell and of the l th M atom. The vector $\pm\vec{d}$ gives the position of the ends of the dumbbell with respect to its center of mass; the direction of \vec{d} is specified by the polar angles (θ, φ) . The particles r (for $r = n$ or l) are allowed to vibrate around their equilibrium positions \vec{X}_r , with center-of-mass displacements $\vec{u}_r = \vec{R}_r - \vec{X}_r$. Consequently, expression (1) represents a translation- and orientation-dependent potential (labeled OT). Summing over all pairs (n, l) and taking only nearest-neighbor interactions (as indicated by the prime), we write

$$V^{OT} = \sum_{n,l} 'V_{ni}^{OT}.$$

In addition, we consider a purely translational potential

$$V^{TT} = \sum_{n,l} 'V_{ni}^{TT}(|\vec{R}_n^- - \vec{R}_i^+|). \quad (2)$$

The kinetic energy \mathcal{T} is composed of two parts:

$$\mathcal{T} = \sum_r \vec{P}_r^2 / 2m_r + \sum_n \vec{L}_n^2 / 2I, \quad (3)$$

where \vec{P}_r (for $r = n, l$) is the linear (translational) momentum of the r th particle and where \vec{L}_n is the angular momentum of the n th dumbbell; m_r and I denote, respectively, the mass of the r th particle and moment of inertia of the dumbbells.

The total Hamiltonian is now given by $H = T + V^{OT} + V^{TT}$. Next, the potential energies V^{OT} and V^{TT} are expanded in terms of translational displacements \vec{u}_r (for $r = n, l$). Thereby we restrict ourselves to terms of zeroth and first order in \vec{u}_r for the contributions arising from V^{OT} . The

zeroth-order term of V^{OT} is proportional to cubic harmonics of order four and six: $V^0 = \alpha_4 K_4(\theta, \varphi) + \alpha_6 K_6(\theta, \varphi)$, and represents an extension of the well-known Devonshire potential.^{7a} The first-order terms are proportional to spherical harmonics of order $l = 2$. As far as the pure translational part V^{TT} is concerned, we restrict ourselves to second-order contributions in \vec{u}_r . Since we are only interested in the elastic behavior, we use Born's long-wavelength expansion¹⁰ and transform all translations to the center-of-mass coordinates of the unit cell. The total Hamiltonian now reads $H = H^T + H^O$, where

$$H^T = \sum_{\vec{k}, i, j} \left(\frac{p_i^\dagger(\vec{k}) p_i(\vec{k})}{2m} + \frac{1}{2} M_{ij}(\vec{k}) s_i^\dagger(\vec{k}) s_j(\vec{k}) \right), \quad (4)$$

$$H^O = \sum_{\vec{k}, i, \alpha} \left(\frac{L^\dagger(\vec{k}) L(\vec{k})}{2I} + i v_{i\alpha}(\vec{k}) Y_\alpha^\dagger(\vec{k}) s_i(\vec{k}) \right) + V^0(\vec{k} = 0). \quad (5)$$

Here, the dagger denotes Hermitian conjugation; $s_i(\vec{k})$ is the i th component ($i = x, y, z$) of the center-of-mass displacement, and $s_i(\vec{k}) = N^{-1/2} \sum_n \exp[-i\vec{k} \cdot \vec{X}(n)] s_i(n)$, where n runs over all N unit cells; m is the total mass per unit cell and $m = m_+ + m_-$; $M_{ij}(\vec{k})$ arises from the second-order term of the translational potential V^{TT} ; $p_i(\vec{k})$ is the translational momentum conjugate to $s_i(\vec{k})$. In Eq. (5), the Y_α , with $\alpha = 1-5$, represent linear combinations of spherical harmonics Y_l^m of order $l = 2$: $Y_1 = Y_2^0$; $Y_2 = \sqrt{3/2}(Y_2^2 + Y_2^{-2})$; $Y_3 = i(Y_2^2 - Y_2^{-2})$; $Y_4 = (Y_2^1 - Y_2^{-1})$; and $Y_5 = -i(Y_2^1 + Y_2^{-1})$. The coupling coefficients $v_{i\alpha}$ are found to be

$$v = \frac{2a}{\sqrt{m}} \begin{pmatrix} k_x A & -k_x A & k_y B & 0 & k_z B \\ k_y A & k_y A & k_x B & k_z B & 0 \\ -2k_z A & 0 & 0 & k_y B & k_x B \end{pmatrix}, \quad (6)$$

with $\alpha = 1-5$ and $i = x, y, z$. Here the x, y , and z directions are taken along the cubic axes of the crystal. The coefficients A and B are functions of the potential parameters C_1 and C_2 , as well as of d and a . The important point here is that vY^\dagger is linear in both the rotational coordinates Y_α^\dagger (or Y_α) and the translations s_i .

The Hamiltonian H is used to calculate the elastic constants. We first calculate the displacement susceptibility¹¹ $(s_i(\vec{k}), s_j(\vec{k})) = (D^{-1})_{ij}$. Here we write $(A, B) = \langle\langle A^\dagger; B \rangle\rangle_0$ for the static limit of the retarded Green's function $\langle\langle A^\dagger; B \rangle\rangle_\omega = -i \int_0^\infty dt e^{-i\omega t} \times \langle [A^\dagger(t), B(0)] \rangle$. The corresponding equation of motion reads as follows¹²:

$$\omega \langle\langle A^\dagger; B \rangle\rangle_\omega = \langle [A^\dagger, B] \rangle + \langle\langle [A^\dagger, H]; B \rangle\rangle. \quad (7)$$

We apply this result twice to $\langle\langle s^\dagger; s \rangle\rangle_\omega$, use the commutation rules $[s_i^\dagger, p_j] = i\delta_{ij}$ and $[s^\dagger, s] = [p^\dagger, p] = 0$, and finally set $\omega = 0$. We then obtain

$$D^{-1} = M^{-1} - iM^{-1}v(Y, s). \quad (8)$$

Applying the same procedure to $\langle\langle s^\dagger; Y \rangle\rangle_\omega$, we find

$$(Y, s) = i\chi^R v^\tau M^{-1}, \quad (9)$$

where v^τ is the transpose of v , and $(\chi^R)_{\alpha\beta} = (Y_\alpha, Y_\beta)$ is the static orientational susceptibility matrix; and consequently Eq. (8) can be rewritten as

$$D = (1 + QM^{-1})^{-1}M, \quad (10)$$

where $Q = v\chi^R v^\tau$. Knowing D , we identify the elastic constants according to $D_{ij} = (V_z/m)C_{in,ji} \times k_n k_i$ (where V_z is the volume of the unit cell). In the absence of coupling to rotations ($v = 0$), Eq. (10) reduces to the bare elastic constants $M_{ij} = (V_z/m)C_{in,ji}^0 k_n k_i$. Using Voigt's notation for the elastic constants and taking $\vec{k} = (0, 0, k)$, we find from Eq. (10) that

$$c_{44} = (m/V_z)D_{11}(k)/k^2 = c_{44}^0/(1 + B'^2\chi_{44}^R), \quad (11a)$$

$$c_{11} = (m/V_z)D_{33}(k)/k^2 = c_{11}^0/(1 + 4A'^2\chi_{11}^R), \quad (11b)$$

where $A' = 2aA(V_z c_{11}^0)^{-1/2}$ and $B' = 2aB(V_z c_{44}^0)^{-1/2}$.

In order to calculate χ^R , we use the physical picture that the interaction between rotation and translation in Eq. (5) leads to an effective interaction between rotating molecules. This concept of an effective interaction between order-parameter variables which is mediated by the lattice deformations is well known in compressible Ising models,¹³ hydrogen in metals,¹⁴ and Jahn-Teller systems.¹⁵ Using methods known from Refs. 13–

15, we find

$$V_{\text{eff}} = -\frac{1}{2} \sum_{\vec{k}} Y_\alpha^\dagger(\vec{k}) C^{\alpha\beta}(\vec{k}) Y_\beta(\vec{k}), \quad (12)$$

where $C = v^\tau M^{-1}v$. Besides this interaction, the rotating molecules experience the single-particle Devonshire potential V^0 [see Eq. (5)]. Using molecular-field theory with the potential $V = V_{\text{eff}} + V^0$, we find

$$\chi_{44}^R = y/(T - y\delta); \quad \chi_{11}^R = x/(T - x\gamma), \quad (13)$$

with $\delta = B'^2$ and $\gamma = 4A'^2$ being eigenvalues of the effective interaction, and T is the temperature; x and y are defined by

$$\begin{aligned} x &= \text{Tr}[\exp(-V^0/T)Y_3^*Y_3]/\text{Tr}\exp(-V^0/T), \\ y &= \text{Tr}[\exp(-V^0/T)Y_1^*Y_1]/\text{Tr}\exp(-V^0/T). \end{aligned} \quad (14)$$

Obviously, the temperature-dependent single-particle effects represented by x and y , describing the molecular reorientations in the octahedral potential V^0 , affect drastically the temperature dependence of χ^R . Combining Eqs. (13), and (11a) and (11b), we find

$$c_{44} = c_{44}^0(1 - y\delta/T); \quad c_{11} = c_{11}^0(1 - x\gamma/T). \quad (15)$$

We have calculated c_{44} and c_{11} from Eq. (15) using $a = 3.15 \text{ \AA}$, $d = 0.6 \text{ \AA}$, $C_2 = 3.3 \text{ \AA}^{-1}$, $C_1 = 1.34 \times 10^{-9} \text{ erg}$, $c_{44}^0 = 0.25 \times 10^{11} \text{ dyn cm}^{-2}$, and $c_{11}^0 = 3.5 \times 10^{11} \text{ dyn cm}^{-2}$. We find that $\delta y > \gamma x$ and $T_c = 154 \text{ K}$ is the solution of $y(T)\delta = T$. At T_c , χ_{44}^R diverges and c_{44} vanishes. The values of C_1 and C_2 are chosen to determine T_c but not to yield a best fit for c_{44} and c_{11} ! Experiment and theory are compared in Figs. 1 and 2. The temperature behavior of y and x is shown in Fig. 3.

The results of this Letter are summarized as follows: The repulsive-overlap-force model [Eq.

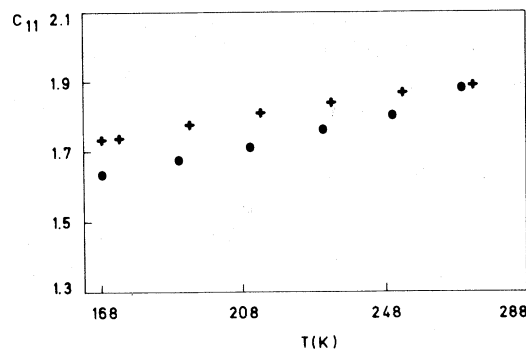


FIG. 1. Increase of c_{11} with T (linear scale). Crosses, experiment (Ref. 4); dots present theory. Units are $10^{11} \text{ dyn cm}^{-2}$.

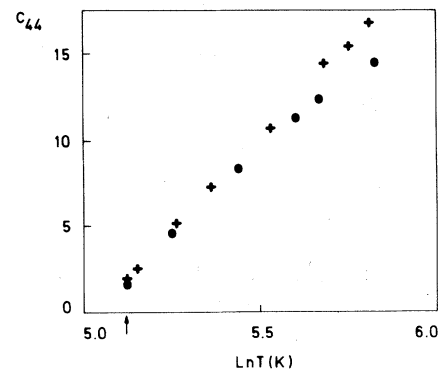


FIG. 2. Increase of c_{44} with T (logarithmic scale). Crosses, experiment (Ref. 4); dots present theory. Units are 10^9 dyn cm^{-2} .

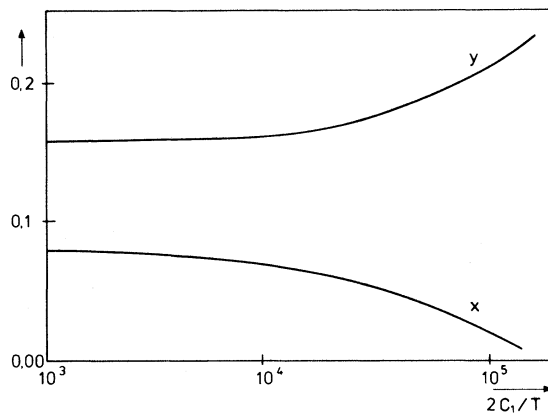


FIG. 3. Temperature variation of single-particle susceptibilities.

(1)] leads to the octahedral Devonshire potential and to an interaction of translations and rotations. This interaction provides an effective coupling between molecular reorientations and drives the orientational phase transition. The single-particle susceptibilities x and y are crucial in determining T_c and affect the temperature behavior of the elastic constants.

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Intramolecular and Surface Vibratory Modes of Butane Adsorbed on Graphite Observed by Inelastic Neutron Scattering^(a)

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Inelastic and elastic neutron scattering have been used to study the dynamics and structure of butane (C_4H_{10}) adsorbed on a graphitized carbon powder at 77 K. In addition to the intramolecular vibrations found in the bulk solid, new surface vibratory modes are observed. A simple model which fits the principal features of the monolayer excitation spectrum suggests an orientation of the adsorbed butane molecule and the location and strength of the bonds to the substrate.

It has been recognized for over a decade that hydrogenous films provide a wide class of adsorbates whose dynamical properties can be studied by inelastic neutron scattering.¹⁻³ Scattered intensities sufficient to study the dynamics of submonolayer films result not only from the

large incoherent cross section of hydrogen for thermal neutrons (~ 80 b) but also the large-amplitude molecular vibrations arising from the small atomic mass. Nevertheless, due in large part to the heterogeneity of the substrates employed, well-defined excitations generally have