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Critical Scattering in Solid CD_4

Alfred Hüller and Werner Press
Institut für Festkörperforschung, Kernforschungsanlage Jülich, Jülich, West Germany
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We have observed a pronounced anisotropy of critical neutron scattering at the 27-K phase transition of solid heavy methane. The anisotropy is due to orientational fluctuations of mainly two-dimensional character. We develop a formalism to treat neutron scattering from orientational fluctuations. Agreement with experiment is reasonable.

Many molecular solids crystallize in a plastic phase which is characterized by a regular lattice for the molecular centers and by disorder with respect to molecular orientations. In this paper we report detailed observations of critical fluctuations at a transition from a plastic to an orientationally ordered phase. We have studied the I/II phase change of solid CD_4. The critical nature of this transition has been shown recently.[1]

Phase I is the plastic phase ($89.7 \geq T \geq 27.0$ K). In phase II ($27.0 \geq T \geq 22.1$ K) six of eight molecules are (antiferrorotationally) ordered.[1,2] For both phases the center-of-mass lattice is fcc. In the high-temperature phase, Bragg scattering results from the center-of-mass structure only. Additional reflections in the ordered phase are due to the long-range orientational order. Critical scattering, originating from orientational fluctuations, has been directly observed in the plastic phase by neutron diffraction and peaks at positions which become the superstructure reflections of CD_4 II. The measured intensity is remarkably *anisotropic*, appearing nearly as lines of strong scattering aligned in $\langle 1, 1, 1\rangle$ directions. We conclude that orientational correlations in methane are predominantly *two-dimensional.*

We have developed a new expression for the coherent neutron scattering of a system of molecules with orientational correlations. Making use of the symmetry of the molecules, the problem is reduced to the calculation of a simple correlation function which is evaluated in the Ornstein-Zernike approximation. We find remarkable agreement with our experimental results.

A large single crystal of about 20 cm^3 was used throughout the experiment. A mosaic spread of 8 min full width at half-maximum (FWHM) was determined from the rocking curve of a Bragg reflection. Additional crystallites contained in the sample volume were smaller by at least a factor 10. The measurements have been performed with a three-axis spectrometer at the FRJ-2 reactor in Jülich. Quasielastic intensities were measured at an incoming neutron energy $E_i = 24.5$ meV, monochromatized by a Ge-311 crystal with an analyzer set at the elastic position (energy resolution FWHM = 1.0 meV). From an additional determination of an upper limit to the quasielastic linewidth Γ ($\Gamma \lesssim 0.25$ meV at $T = 27.6$ K) it is evident that an effective integration over energy is taking place. The main axes of the resolution ellipsoid in Q space were calculated to $\Delta Q_x = 0.0075$ Å^{-1} and $\Delta Q_y = 0.0070$ Å^{-1}. A vertical resolution $\Delta Q_z = 0.06$ Å^{-1} at a momentum transfer $Q = 3.2$ Å^{-1} was determined experimentally in the ordered phase. Resolution corrections should be small and thus were omitted.

We have examined the critical scattering in the vicinity of two symmetry-related L points in the $[1, \bar{1}, 2]$ zone of scattering, namely, at $(2.5, 1.5, -0.5)$ and at $(2.5, -0.5, -1.5)$, where the strongest superstructure reflections develop in phase II. As can be seen in Fig. 1, the intensity contours around the two L points look quite different. The scattering intensity [Fig. 1(a)] falls off very slowly along the $[1, \bar{1}, \bar{1}]$ direction, connecting the L point at $(2.5, 1.5, -0.5)$ with its zone center at $(2, 2, 0)$. The equivalent line of high intensity in the neighborhood of the second L point [Fig. 1(b)] is not contained in the $[1, \bar{1}, 2]$ zone, but intersects it at an angle of 70.5°. Thus the two intensity contours are mutually perpendicular to a good approximation and yield detailed information on the spatial distribution of scattering. It has the shape of a cigar with the long axis in the particular $\langle 1, 1, 1\rangle$ direction passing through the L point. The strong anisotropy of critical scattering shows that the orientational correlations are extremely strong in planes perpendicular to the four different $\langle 1, 1, 1\rangle$ directions. Correlations between these planes are weak. Using the relation $\chi(\vec{q}) \propto (1 + \xi_\parallel^2 q_\parallel^2 + \xi_\perp^2 q_\perp^2)^{-1}$ ($\vec{q} = \vec{Q} - 2\pi\vec{\tau}_L$, with components $q_\parallel$ and $q_\perp$ parallel and perpendicular to the relevant $[1, 1, 1]$ direction) for the q-dependent susceptibility, we extract from the measure-

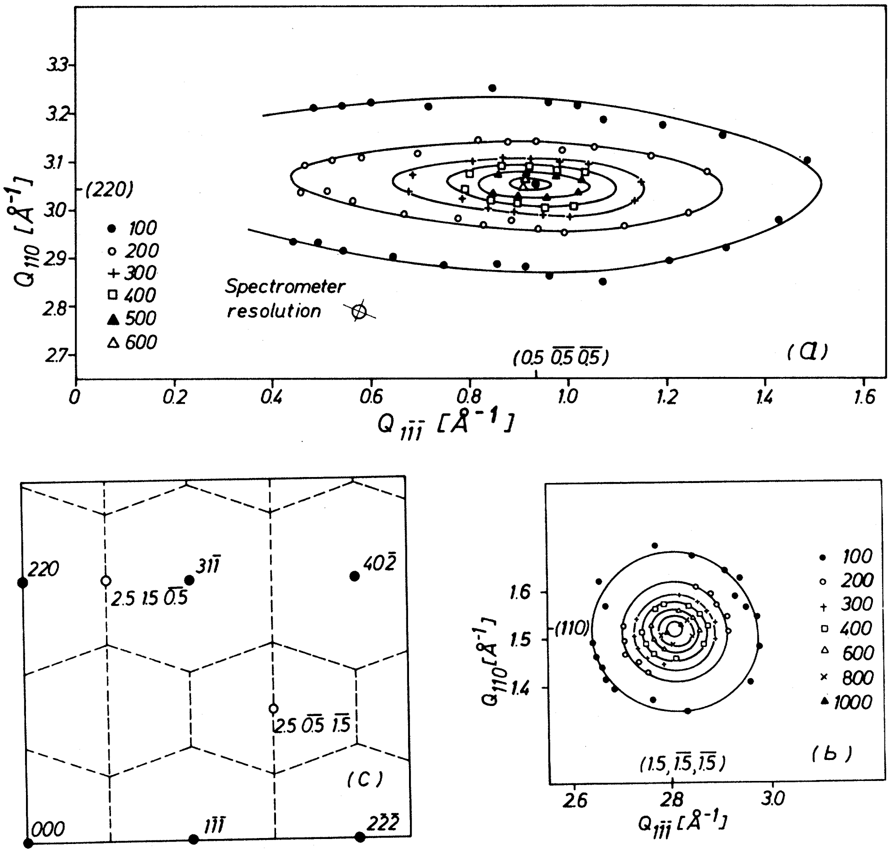

FIG. 1. Critical scattering in CD$_4$ I. (c) Intensity contours in the [1, $\bar{1}$, 2] zone of scattering. At (2.5, −0.5, −1.5) the long axis of intensity is contained in the zone (a); at (2.5, −0.5, −1.5) it is not contained and is 70.5° to the scattering plane (b) (background, 50 counts).

ment (Fig. 1) an intraplane correlation length $\xi_\perp \approx 20$ Å and an interplane correlation length $\xi_\parallel \approx 5$ Å for $T = 27.6$ K. The fluctuations are therefore essentially two-dimensional, similar to the behavior of some antiferromagnets, e.g., K_2NiF_4[3] or $KFeF_4$.[4] Contrary to the magnetic example, however, where strong correlations occur in one set of planes only, we have to consider four sets of equivalent planes in the case of methane. The contours (FWHM) of the resolution ellipsoid in the (1, $\bar{1}$, 2) zone are also given in Fig. 1(a). The difference in peak intensity at the two L points is due to vertical resolution.

To calculate the critical scattering, we start from the coherent scattering function integrated over energy. For an assembly of molecules, $S(\vec{Q})$ is given by the equal-time correlation function

$$S(\vec{Q}) = N^{-1}\langle \textstyle\sum_{ij} \exp(i\vec{Q}\cdot\vec{R}_i) \int \exp(i\vec{Q}\cdot\vec{r}_i)\, a_i(\vec{r}_i)\, d^3r_i \exp(-i\vec{Q}\cdot\vec{R}_j) \int \exp(-i\vec{Q}\cdot\vec{r}_j)\, a_j(\vec{r}_j)\, d^3r_j\rangle. \tag{1}$$

Here N denotes the number of molecules, $\hbar\vec{Q}$ the momentum transfer, $\vec{R}_i$ the position of the center of the ith molecule, and $a_i(\vec{r}_i)$ the coherent scattering-length density of the ith molecule at a distance $\vec{r}_i$ from its center. We introduce a primed coordinate system fixed in the molecule and expand $a(\vec{r}\,')$ into tetrahedral harmonics, which are linear combinations of spherical harmonics and form an irreducible representation of the tetrahedral group,

$$a(\vec{r}\,') = \sum_{l=0}^{\infty} \sum_{\mu=1}^{2l+1} \alpha_{l\mu}(r') T_{l\mu}(\theta', \varphi'). \tag{2}$$

To get $a(\vec{r})$, the scattering-length density in the coordinate system of the crystal, we use the transformation properties of the tetrahedral harmonics,

$$T_{l\mu}(\theta', \varphi') = \sum_{\tau=1}^{2l+1} T_{l\tau}(\theta, \varphi) U_{\tau\mu}^{(l)}(\omega). \tag{3}$$

Equation (3) is the definition of the tetrahedral rotator functions $U_{\tau\mu}^{(l)}(\omega)$. They depend on the Euler angles (here denoted collectively by ω) which relate the unprimed coordinate system to the primed one. Expanding $\exp(i\vec{Q}\cdot\vec{r})$ into tetrahedral harmonics as well and performing the angular integrations in (1), we obtain

$$S(\vec{Q}) = \frac{1}{N} \sum_{l, l'=0}^{\infty} i^l(-i)^{l'} \sum_{\tau, \mu=1}^{2l+1} \sum_{\tau', \mu'}^{2l'+1} A_{l\mu}(Q_0) A_{l'\mu'}(Q_0) T_{l\tau}(\theta_0, \varphi_0) T_{l'\tau'}(\theta_0, \varphi_0)$$
$$\times \langle \sum_{ij} \exp(i\vec{Q}\cdot\vec{R}_i)\, U_{\tau\mu}^{(l)}(\omega_i) \exp(-i\vec{Q}\cdot\vec{R}_j)\, U_{\tau'\mu'}^{(l')}(\omega_j)\rangle, \tag{4}$$

where Q_0, θ_0, and φ_0 are the polar coordinates of $\vec{Q}$ and

$$A_{l\mu}(Q_0) = \int j_l(Q_0 r) a_{l\mu}(r) r^2\, dr;$$

the $j_l(Q_0 r)$ are spherical Bessel functions. For simplicity we neglect the thermal motion of the molecular centers. The problem is then reduced to the calculation of the correlation function $\langle U_{\tau\mu}^{(l)}(\omega_i) \times U_{\tau'\mu'}^{(l')}(\omega_j)\rangle$. The trivial term $\langle U_{11}^{(0)}(\omega_i) U_{11}^{(0)}(\omega_j)\rangle = 1$ is responsible for the reflections from the center-of-mass structure. This intensity is the same above and below T_c, in analogy to the nuclear reflections in antiferromagnetic solids.

A restriction to the nearest-neighbor octupole-octupole interaction leads to the model Hamiltonian studied by James and Keenan,[2] which contains only tetrahedral harmonics of order $l = 3$,

$$\mathcal{H} = \frac{I_3^2}{2R^7} \sum_{i, j=1}^{N} \sum_{\alpha, \beta=1}^{7} U_{\alpha 1}^{(3)}(\omega_i) C_{\alpha\beta}^{ij} U_{\beta 1}^{(3)}(\omega_j), \tag{5}$$

where I_3 is the octupole moment and R is the nearest-neighbor distance. We evaluate the correlation function in the Ornstein-Zernike approximation, which is the only manageable approach to a system as complex as a molecular crystal, and obtain

$$S(\vec{Q}) = \sum_{\alpha, \beta=1}^{7} F_{\alpha\beta}(\vec{Q}) kT \sum_{\lambda=1}^{7} B_{\alpha\lambda}^{-1}(\vec{q}) \left[kT + \frac{I_3^2}{7R^7}\Gamma_\lambda(\vec{q})\right]^{-1} B_{\lambda\beta}(\vec{q}), \tag{6}$$

where we have introduced

$$F_{\alpha\beta}(\vec{Q}) = A_{31}^2(Q_0) T_{3\alpha}(\theta_0, \varphi_0) T_{3\beta}(\theta_0, \varphi_0).$$

The $\Gamma_\lambda(\vec{q})$ are eigenvalues of $C_{\alpha\beta}(\vec{q})$, the Fourier transform of $C_{\alpha\beta}^{ij}$, and $B_{\lambda\beta}(\vec{q})$ is the matrix which diagonalizes $C_{\alpha\beta}(\vec{q})$. The lowest eigenvalue $\Gamma_7(\vec{q}_L) = -\frac{357}{4}$ occurs at $\vec{q}_L = (2\pi/a_0)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (a_0 is the lattice constant) and is responsible for the phase transition at $kT_c = \frac{51}{4} I_3^2/R^7$. In the vicinity of the (1, 1, 1) direction the dispersion of the lowest eigenvalue can be approximated by

$$\Gamma_7(\vec{q}) = -\frac{357}{4} + 12 b_\parallel^2 \sin^2(\tfrac{1}{6}\sqrt{3}\, a_0 q_\parallel) + b_\perp^2 (a_0 q_\perp)^2, \tag{7}$$

where $b_\parallel = 0.35$ and $b_\perp = 3.25$. With these numbers inserted into (6), a theoretical anisotropy of the critical scattering, $b_\perp/b_\parallel = 9$, results. It is not surprising that this differs with our experimental anisotropy $\xi_\perp/\xi_\parallel = 4$. In the Hamiltonian (5) we have neglected the octupole-octupole interaction of all but nearest-neighbor molecules and the effect of higher-order multipole moments. These terms are certainly small. As, however, the calculated dispersion of $\Gamma_7(\vec{q})$ along $\langle 1, 1, 1\rangle$ almost vanishes, the contribution of the neglected terms to $b_\parallel$ becomes crucial. Besides the reported anisotropy, an additional asymmetry of the intensity contours in Fig. 1(a) is visible. It is due to the rapidly varying form factor $\sum_{\alpha\beta} F_{\alpha\beta}(\vec{Q}) \times B_{\alpha 7}^{-1}(\vec{q}) B_{7\beta}(\vec{q})$, which modulates (and shifts) the otherwise elliptic intensity contours. We have shown that the critical fluctuations in solid methane are largely two-dimensional in character and we have presented a formalism by which we can explain our experimental results to a remarkable extent. This approach appears to be promising for the calculation of critical scattering not only at transitions from plastic to orientationally ordered phases, but may also apply in other order-disorder transitions of molecular crystals, e.g., in the ammonium halides.

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Role of Disorder in a Class of One-Dimensional Conductors*

E. Ehrenfreund,† S. Etemad, L. B. Coleman, E. F. Rybaczewski, A. F. Garito, and A. J. Heeger
Laboratory for Research on the Structure of Matter and Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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It is shown that the class of one-dimensional "metallic" conductors based on tetracyanoquinodimethan is not to be viewed as dominated by disorder. The experimental measurements of the electrical conductivity, magnetic susceptibility, and nuclear relaxation rates are each inconsistent with the disorder model. It is concluded that the electronic properties of these tetracyanoquinodimethan salts are primarily determined by band and interaction effects.

In a recent paper Bloch, Weissman, and Varma (BWV)[1] have asserted that the electronic properties of the highly conducting tetracyanoquinodimethan (TCNQ) salts are the result of lattice disorder. We demonstrate in this Letter that this assertion is untenable, that the disorder theory as applied to these one-dimensional (1D) conductors is not consistent with the experimental results, and that in the TCNQ salts (where sufficient data are available) the electronic properties are primarily determined by band and interaction effects.

The assertion of BWV is based upon the following arguments: (i) Disorder causes localization of wave functions in 1D, and (ii) the low-temperature conductivity of the TCNQ salts can approximately be fitted by $\log\sigma \sim (T_0/T)^{1/2}$ as derived for a disordered 1D system by analogy with the earlier work on 3D systems.[2-4] It is further claimed that the high-temperature conductivity arises not from a metal, but is determined by classical diffusion through the localized states, such that $\sigma = \sigma_D = (nNe^2/k_BT)\nu_{ph}a^2$, where n is the density of electrons on the chain, N is the number of chains per unit area, ν_{ph} is characteristic phonon frequency which drives the diffusion, and a is the lattice constant. The disorder, according to BWV, arises from the long-range Coulomb interaction of $(TCNQ)^-$ with the asymmetric charge distribution in the randomly oriented cation donor molecules.

Given the presence of random potentials, the question of the possible importance of disorder must be treated more quantitatively. If Δ_d is the rms disorder potential and W is the bandwidth in absence of disorder, then the ratio W/Δ_d describes the relevant regimes.[5] For $W/\Delta_d \gg 1$, disorder plays only a peripheral role (band tailing, etc.). Indeed, even in this case the "band" wave functions are strictly speaking not of infinite extent; this is irrelevant, however, as crystal imperfections and defects will clearly set an upper limit to the extent of wave functions in real samples. In this limit one can view such systems as long but finite chains with electrons interacting via the electron-electron Coulomb interaction as described previously.[6,7] In the opposite limit, $W/\Delta_d < 1$, the disorder would dominate and the wave functions would be localized to approximately a single lattice site. We give below analyses of the conductivity, magnetic susceptibility, and nuclear relaxation time; in each case the data are inconsistent with the disorder model.

The strongest argument of BWV arises from the low-temperature conductivity. If one assumes dominance of disorder, the low-temperature conductivity would result from the variable-range hopping mechanism proposed by Mott.[2] In 1D the problem can be simply viewed as a diffusion process. The conductivity can be written as σ