Critical Slowing Down of Orientational Fluctuations in a Plastic Crystal

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For the first time a critical slowing down of orientational fluctuations on approaching the order-disorder transition of a plastic crystal has been detected. The observed inverse relaxation rates Γ^{-1} in solid CD_4 range from 10^{-11} sec (11° above $T_0 = 27$ K) to 2.5×10^{-10} sec (close to T_0). The temperature dependence of Γ can be fitted by a power law with an exponent $\rho = 1.13 \pm 0.13$. For the q dependence of Γ an exponent $z = 1.90 \pm 0.14$ is found close to T_0.

Orientational order-disorder transitions in molecular crystals are attracting more and more interest. They may serve, for example, as new tests of the universality of predictions[1] in the field of critical phenomena. Orientational order-disorder transitions occur in the liquid as well as in the solid state. In the latter case, we may qualitatively distinguish between two extremes, namely (i) transitions in which the disordered phase is characterized by a discrete molecular orientational distribution, and (ii) transitions which start out from an almost continuous orientational distribution. The one extreme is represented by the ammonium halides,[2] the other by the so-called plastic crystals, e.g., solid methane.[3,4] Looking at the microscopic properties of these phase changes one notices a striking analogy with magnetic phase transitions.[5,6] In the case of solid CD_4 the analogy is with the paramagnetic-to-antiferromagnetic transition.[7]

CD_4, which solidifies at 89 K, has an orientationally disordered high-temperature phase I[3,4]; the center-of-mass structure is fcc [space group $Fm3m$; lattice constant a_0(30 K) = 5.84 Å]. At T_0 = 27.0 K a transition to an anti–ferro-orientational phase II occurs,[3,8] without change of the center-of-mass structure. The interactions between the electrostatic octupole moments of the methane molecules give rise to the antiorder on six of the eight sublattices; the other two sublattices remain disordered in phase II (spacegroup $Fm3c$).

Recently, static critical phenomena in CD_4 have been investigated experimentally and theoretically; in particular, the orientational order parameter(s)[9] and static orientational correlations[10,11] have been determined. The critical scattering above T_0 was found to be strongly an-

isotropic with high intensity in the $\langle 111 \rangle$ directions. An anisotropy $A = \xi_\perp / \xi_\parallel = 4$ was found experimentally[10]; here $\xi_\perp$ and $\xi_\parallel$ are the correlation lengths perpendicular and parallel to $\langle 111 \rangle$, respectively. The present study was performed in order to shed some light on the dynamical aspects of the phase transition. The experiments were carried out at the high-flux reactor in Grenoble with a three-axis spectrometer. Two phenomena which have rather direct analogs in anisotropic antiferromagnets were the subjects of this investigation: (i) the temperature dependence of librational excitations in phase II (spin waves), and (ii) the temperature and wave-vector dependence of the energy width of critical fluctuations above T_0 (dynamics of the staggered susceptibility). Below T_0 we expect librational excitations with essentially the same temperature dependence as the orientational order parameter[8] (the octupolar component of ordering). Assuming (a) rigid molecules, (b) negligible coupling to the center-of-mass motion, as well as (c) negligible coupling to the rotational motion of the disordered molecules, there are eighteen modes of purely rotational character involving ordered molecules. In order to take advantage of degeneracies, the measurements were restricted to points of high symmetry.

No well-defined librational excitations were observed, even at the lowest accessible temperature in phase II ($T \gtrsim 22.1$ K). We may conclude that the modes are undetectable either (i) because the inelastic structure factors are too small, or (ii) because assumptions (b) and (c) do not hold—that is, the modes are severely damped by libron-phonon coupling or by a coupling to the rotational motion of the disordered molecules.

Quantitative estimates of the structure factors[12] (in the harmonic approximation) make us believe that (ii) is true.

Apart from propagating modes connected with the order parameter there are orientational fluctuations in both phases. In the disordered phase I the observation of critical fluctuations is not impeded by the presence of superlattice reflections. As in antiferromagnetic systems, where the staggered magnetization is not conserved, the "staggered orientation" is not a conserved quantity. Hence, the decay of orientational fluctuations should be of the relaxation type. We may expect a "critical slowing down" of the orientational fluctuations—that is, a relaxation rate Γ which ideally (in a continuous transition) approaches zero at the critical point. Assuming an exponential decay $\exp(-\Gamma t)$ of the correlated regions, we may write the scattering function

$$S(\vec{Q}, \omega) = S_1(\vec{Q}) \frac{\Gamma(\vec{q}, T)/\pi}{\Gamma(\vec{q}, T)^2 + \omega^2} . \tag{1}$$

Here ω and $\vec{Q}$ are the energy transfer and momentum transfer of the neutrons, respectively, and $\vec{q} = \vec{Q} - \vec{Q}_L$ is the distance from a zone-boundary L point, where the distortion to phase II occurs. $S_1(\vec{Q})$ is the static scattering function. An explicit expression for it has been derived in Ref. 10 in the molecular-field approximation.

The measurements require high energy resolution at a relatively large incoming energy E_i. A large E_i is necessary because the relevant L point [with Miller indices $(531)/2$] demands a
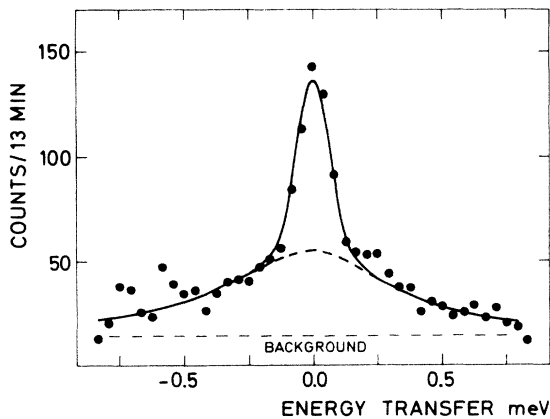
scattering vector as large as $Q_L = 3.18$ Å^{-1}. The actual setup used three Cu(220) crystals for monochromatizing and analyzing the neutrons, with $E_i = 13.7$ and 14.8 meV; higher order neutrons were removed with a pyrolytic graphite filter. Energy resolutions (full width at half-maximum) of 0.104 ± 0.05 and 0.153 ± 0.07 meV, respectively, were determined experimentally. Throughout the experiment a $[1\bar{1}2]$ zone of a methane single crystal (mosaic 42 min) was used. This zone contains two different types of L points in which the corresponding $\langle 111 \rangle$ direction is either contained in the zone of scattering or almost perpendicular to it. The temperature dependence of $\Gamma(q = 0, T)$ was studied at $\vec{Q}_L = (5\bar{1}3)/2$. A typical constant-$\vec{Q}$ scan is shown in Fig. 1. At this temperature (38.2 K), far above T_0, the critical scattering is well separated from the elastic incoherent background, the latter having the Gaussian-shaped response centered at $E = 0$ and a width due to instrumental resolution. The half width at half-maximum of the critical scattering at this temperature is 0.38 ± 0.05 meV, corresponding to a relaxation time of 10^{-11} sec. This is only slightly slower than relaxation times observed in magnetic systems at the same reduced temperature.[13]

In the vicinity of T_0, four-dimensional (numerical) resolution corrections become important, and have been performed essentially in the way reported in Ref. 13, for example. Figure 2 shows resolution-corrected relaxation rates as a function of temperature. In the range of 38 to 27 K $(0T_0)$ a "critical slowing down" from $\tau_{q0} = 1/$
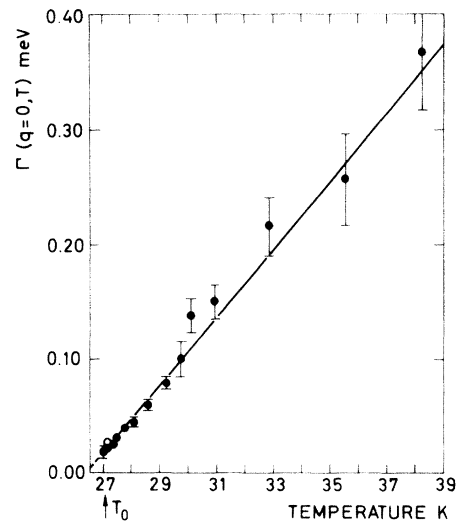

FIG. 1. Constant-$\vec{Q}$ scan in CD_4 I ($T = 38.2$ K) at the L point $[\vec{Q}_L = (5\bar{1}3)/2]$. The incoherent elastic scattering and the critical scattering are well separated ($E_i = 14.8$ meV). The former is Gaussian-shaped with instrumental width; the latter has a Lorentzian shape with a half width $\Gamma(q = 0, T = 38.2$ K$) = 0.38 \pm 0.05$ meV. The Lorentzian is shown dashed in the vicinity of $E = 0$.

FIG. 2. Relaxation rate $\Gamma(q = 0, T)$ of orientational fluctuations in CD_4 I at $Q = Q_L$. The error bars shown include the uncertainty due to the statistical error of the instrumental resolution.

$\Gamma(q=0) = 10^{-11}$ sec to $\tau_{q_0} = 2.4 \times 10^{-10}$ sec is observed: that is, the relaxation rate Γ diminishes by a factor of about 25. To our knowledge this is the first time that "critical slowing down"[14] of orientational fluctuations in a plastic crystal has been observed. Figure 2 also shows that the phase transition CD_4 I/II exhibits a small discontinuity at T_0 and hence is of first order[11]: The critical quantities do not really diverge at T_0.

Fitting the experimental results shown in Fig. 2 with $\Gamma(q=0, T) \sim [(T - \overline{T})/\overline{T}]^\rho$ one obtains an extrapolated transition temperature $\overline{T} = 26.24 \pm 0.23$ K and an exponent $\rho = 1.13 \pm 0.13$. This latter value is slightly above the mean-field value $\rho = \gamma = 1$ (for $\rho = 1$, $\overline{T} = 26.46 \pm 0.07$ K). By integrating $S(\vec{Q}, \omega)$ over energy the static susceptibility $\chi(q=0, T)$ may be evaluated and also fitted by a power law. The result is $\gamma = 1.13 \pm 0.10$ and $\overline{T} = 26.30 \pm 0.16$ K. In the hydrodynamic regime $(q \ll 1/\xi)$ we consequently have $\Gamma(q=0, T) \sim \chi(q=0, T)^{-1}$. In order to test the validity of the relation $\Gamma(\vec{q}, T) \sim \chi(\vec{q}, T)^{-1}$ in the critical regime $(q > 1/\xi)$, further measurements were done at $T = 27.12$ K; i.e., close to T_0. For the q dependence of the relaxation rate, we find in a direction perpendicular to $\langle 111 \rangle$

$$\Gamma(q_\perp, T \simeq T_0) = \Gamma_0 + a(T_0) q_\perp{}^z \qquad (2)$$

with $z = 1.90 \pm 0.14$; i.e., very close to 2 [for $z = 2$, $a(T) = 10.5 \pm 0.5$]. Similarly we find for the $\langle 111 \rangle$ direction

$$\Gamma(q_\parallel, T \simeq T_0) = \Gamma_0 + a'(T_0) A^2 c^2 \sin^2(q_\parallel/c). \qquad (3)$$

Here $A = 3.8$ represents the anisotropy of the critical intensity—it agrees with the result of the former static measurement[10] and confirms the predominantly two-dimensional character of the fluctuations; $c = (2\pi\sqrt{3})/a_0$ and $a'(T_0) \simeq a(T_0)$. Putting things together, we find that in both regimes $\Gamma(\vec{q}, T)$ can be described by

$$\Gamma(\vec{q}, T) = a(T)[\xi^{-2}(T) + q_\perp{}^2 + A^2 c^2 \sin^2(q_\parallel/c)], \qquad (4a)$$

$$= \Lambda/\chi(\vec{q}, T); \qquad (4b)$$

Λ is a transport coefficient, which here appears to be regular at the transition point. This is in agreement with van Hove's original postulate,[14] that Λ remains finite at the critical point. Such behavior is also found in anisotropic antiferromagnets[15,16] which are analogous to CD_4 in various respects. In isotropic magnets, on the other hand, Λ is not regular at the transition point, as it depends on critical quantities.[15,16] It may be noted, finally, that our results are in agreement with the predictions of dynamical scaling.[15] A full account of this investigation will be published elsewhere.

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