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Order-disorder phase transition in potassium thiocyanate

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The order-disorder phase transition in KSCN near 142 °C, which is connected with the head-tail orientation of the linear SCN molecules, is investigated by diffuse-neutron-scattering techniques. The results show a transition from a long-range-ordered structure to a short-range-ordered state which persists up to temperatures near the melting point. Above T_c near the (100) superlattice point, a Lorentzian intensity distribution is observed whose temperature dependence shows a mean-field behavior. The short-range-ordered state is described by an ensemble of ordered microdomains.

I. INTRODUCTION

KSCN undergoes a phase transition from a high-temperature tetragonal structure to a low-temperature orthorhombic phase near 142 °C.[1] As shown by x-ray-diffraction data, the transition is connected with the head-tail ordering of the linear SCN molecules.[2] In the low-temperature orthorhombic phase, the SCN molecules show an antiferroelectric ordered arrangement. Early specific-heat measurements revealed a λ-shaped anomaly at T_c and led to the conclusion that the transition is of second order.[3] Recent birefringence measurements in the ordered phase found, however, a steep decrease near T_c and a small hysteresis suggesting the presence of a first-order transition.[4]

The temperature behavior of the elastic constants[5] investigated by ultrasonic techniques shows a steep variation below the transition temperature, i.e., a decrease of the elastic constants. The softening, however, is small and all elastic constants investigated remain at finite, nonzero values at the transition temperature.

Furthermore, the thermal expansion of the lattice parameter of the low-temperature orthorhombic phase exhibits an anomalous increase below the transition temperature. This increase starts about 20° centigrade below T_c and is most pronounced for the orthorhombic *c* direction, which becomes the tetragonal axis in the high-temperature phase.[1]

Recently, NMR experiments have been done. The results indicate that short-range order persists in a relatively large temperature range above T_c.[8,9]

The reorientation of molecules in crystals generally displays a great variety of structural and dynamical features. In order to get insight into the microscopic mechanisms of molecular reorientation in KSCN, we have performed an experiment by neutron-scattering techniques.

II. EXPERIMENT

The measurements were done on the triple-axis spectrometer VALSE located at a cold neutron guide position of the Laboratoire Léon Brillouin at Saclay. The incident neutron energy was 14.7 meV and a pyrolytic graphite filter was put into the incident beam in order to eliminate the higher-order contamination. Pyrolytic graphite PG (002) crystals were used as monochromator and analyzer, respectively, the collimations were 60 min. Single crystals of KSCN with a mosaic spread of 20 min were used as samples.[11] The diffuse-neutron-scattering investigation was performed from room temperature up to 170 °C which is a few degrees below the melting point of KSCN.

III. DIFFUSE-SCATTERING RESULTS

A. Orthorhombic phase

The measurements started with an investigation of the (c^*,a^*) reciprocal-lattice plane of the orthorhombic phase at room temperature. The crystal was in the ordered state of the low-temperature phase as shown by the presence of sharp superlattice reflections located at the (100) wave vector and equivalent points in reciprocal space. The intensity observed at the superlattice points was in accordance with results of a structure factor calculation for the ordered phase. On heating to 100 °C, almost no changes in the Bragg intensities and in the diffuse scattering in the vicinity of the Bragg reflections could be observed. The first significant changes in the scattering pattern occurred at 125 °C (i.e., at a temperature about 20 °C below the transition temperature), where the sharp superlattice reflections showed an intensity decrease. In addition, a broad diffuse intensity distribution centered at the superlattice points was observed (Fig. 1). No similar scattering feature could be detected in the vicinity of the fundamental Bragg reflections.

On further heating to 130 °C, the superlattice reflections showed again an intensity decrease connected with an increase of the diffuse intensity in the neighborhood of the superlattice points. Within the errors, the broad diffuse intensity distribution can be well described by a Gaussian. In the temperature range below the critical temperature where the diffuse scattering is observed, its intensity increases with increasing temperature but its width in reciprocal space remains unchanged (Fig. 1). The extension of the diffuse scattering is somewhat anisotropic in reciprocal space and is, by a few percent, broader along the c^* direction than along a^*. An evaluation of the integral intensity shows that the intensity which appears as diffuse scattering is roughly equivalent to the corresponding intensity decrease of the sharp superlattice reflections. Furthermore, near 140 °C, where the crystal is near the transition point but still in the ordered phase as borne out by the presence of the superlattice reflections, an exploration near the (002) and (004) fundamental reflections showed the appearance of a Huang-type diffuse scattering.[6] The diffuse scattering is seen in radial scans along the c^* direction and is more intense near the (004) point (Fig. 2). This last feature is a characteristic of distortion scattering. Scans near reflections along the a^* direction give no evidence for the presence of a similar diffuse scattering for the corresponding (200) and (400) reflections.

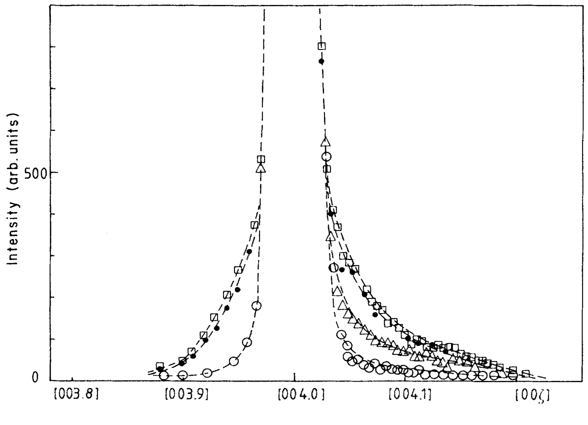

FIG. 2. Elastic distortion scattering observed near the [004] fundamental reflection along [001] at different temperatures near T_c. (○) 50 °C, (●) 135 °C, (□) 142°, (△) 147 °C.

Moreover, the distortion scattering is asymmetric with respect to the fundamental Bragg reflection i.e., the intensities at the $(004)+\mathbf{q}$ side are higher than in the $(004)-\mathbf{q}$ region. From general considerations of Huang scattering theory,[6] this asymmetry characterizes the defect structure responsible for the lattice distortion, i.e., defects which act as compression centers and therefore induce a lattice dilatation (like interstitials) produce a stronger scattering at the $+\mathbf{q}$ side of the Bragg reflection whereas dilation centers (like vacancies) induce more intensity at the $-\mathbf{q}$ side of the reciprocal-lattice point.

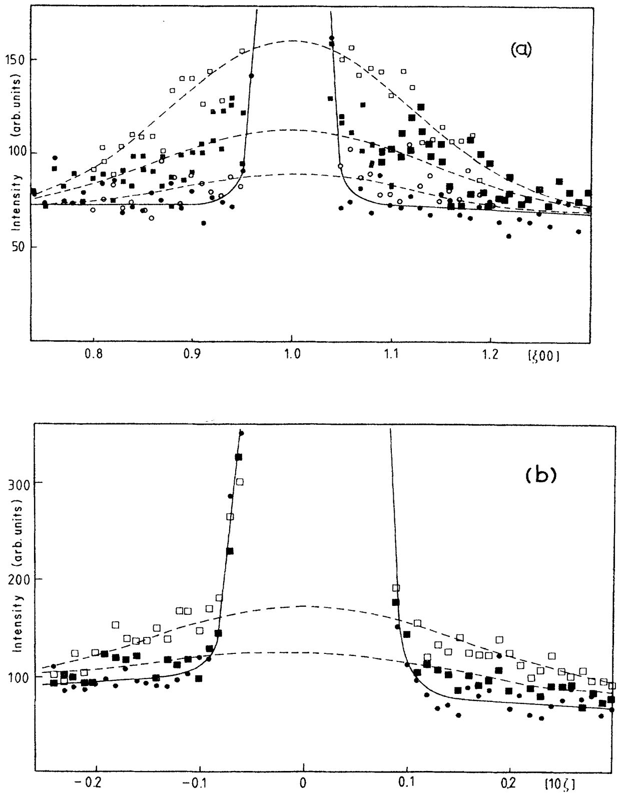

FIG. 1. (a) Diffuse intensity distribution near the [100] superlattice point in scans along the [100] direction at different temperatures below T_c. (●) 75 °C, (○) 125 °C, (■) 135 °C, (□) 140 °C. The lines represent Gaussian fits to the data. (b) The same as in (a) for scans along the [10l] direction. (●) 75 °C, (■) 135 °C, (□) 140 °C.

B. Tetragonal phase

Heating the KSCN crystal above T_c, i.e., to 145 °C, induced a drastic change of the shape of the intensity distribution near the superlattice points (100) and (300), respectively. Below T_c, resolution-limited sharp superlattice reflections were always observed together with a broad Gaussian diffuse intensity distribution. Above T_c, however, a Lorentzian intensity distribution was found (Fig. 3). On further heating, the distribution remained Lorentzian in shape but the intensity decreased, especially near the center of the distribution. The intensity of the

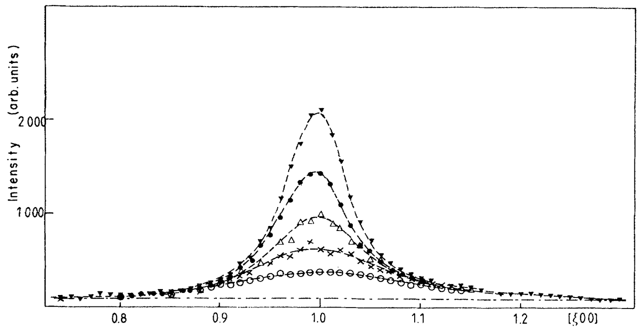

FIG. 3. Intensity distribution around the [100] point in scans along the [100] direction above T_c at different temperatures. The dash-dotted line gives the background level measured in the ordered phase. (▼) 145 °C, (●) 146 °C, (△) 147 °C, (×) 156 °C, (○) 170 °C.

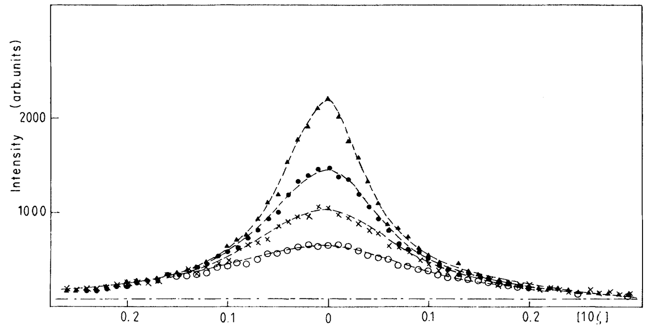

FIG. 4. Intensity distribution in the vicinity of the [100] point for scans along [10ζ] for temperatures above T_c. The dash-dotted line gives the background level measured in the ordered phase. (▲) 145 °C, (●) 147 °C, (×) 150 °C, (○) 156 °C.

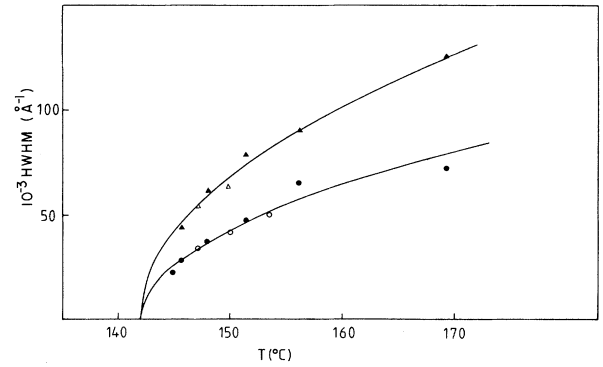

FIG. 5. Fitted values for the widths of the Lorentzian intensity distribution in function of temperature yielding a critical mean-field exponent. Circles, widths along [100]; triangles, widths along [10ζ]; solid symbols, on heating; open symbols, on cooling.

large tails of the Lorentzian remained nearly unchanged. This behavior characterized the temperature dependence of the intensity distribution up to the melting point of KSCN, i.e., near 173 °C The main effect of the temperature variation from T_c to the melting point is an intensity reduction near the center of the Lorentzian. Furthermore, scans along the c^* direction through the (100) point showed essentially the same behavior (Fig. 4). Again, a Lorentzian intensity distribution is observed in the whole temperature range investigated. The width of the Lorentzian, however, along c^* is in absolute units now by about 30% broader than along the a^* direction. This anisotropic behavior is conserved when the temperature changes.

It should be noticed that the measurements were done with the analyzer in the elastic mode. Quasielastic scans through the diffuse intensity distribution give no indication for a quasielastic broadening even at temperatures near 170 °C. The energy width of the intensity distribution near the (100) region was always resolution limited (0.18 and 0.10 THz, respectively). The decrease of elastic intensity observed is therefore not due to a quasielastic broadening and therefore to a dynamical disorder, but indicates an increase of static disorder at higher temperatures.

On cooling, the scattering features were completely reversible within the limits of the experiment. Just below T_c a sharp superlattice reflection was again observed together with the broad Gaussian intensity distribution at the bottom of the reflection. Moreover, a similar distortion scattering was found near the (004) and (002) fundamental reflections. On further cooling to 120 °C, the distortion scattering decreased and finally disappeared. Likewise, the diffuse scattering at the bottom of the (100) reflection disappeared at 120 °C.

IV. FURTHER DATA EVALUATION

The diffuse scattering observed above T_c was fitted to a Lorentzian whose peak intensity and widths along a^* and c^* were determined, respectively. The results are presented in Fig. 5. The figure reproduces the anisotropy in the widths. The fitted values for the widths (w) are in accordance with a critical temperature dependence $w \propto (T-T_c)^\alpha$ yielding a critical exponent $\alpha=\frac{1}{2}$ and indicating, therefore, a mean-field behavior.

An evaluation of the integral intensity below the Lorentzian (Table I) gives essentially a constant value from temperatures just above T_c to temperatures near the

TABLE I. Evaluated integral intensities near the [100] superlattice point above T_c. $I_{\max}$ means the peak intensity, w_1 is the fitted width along the [100] direction, and w_2 corresponds to the width along the tetragonal c direction. With a statistical error of about 10% for the integral intensity, $I=I_{\max}w_1w_2$ (2% for $I_{\max}$, 3–4 % for the widths), the evaluated values scatter by about one σ from the mean value of 3022×10^3. The integral intensity near the superlattice point therefore shows no strong decrease up to the melting point of 172 °C.

T (°C)	$I_{\max}$	w_1 (10^{-3} Å^{-1})	w_2 (10^{-3} Å^{-1})	Iw_1w_2 (10^3 counts)
145.5	2060	28.8	44.6	2646
147.8	1297	37.4	61.3	2973
151.3	846	47.3	78.4	3137
156.1	604	65.3	90.2	3557
169.3	308	72.1	126.0	2798

melting point. This somewhat surprising result is, however, qualitatively in accordance with a direct inspection of the measured intensity distribution, where a temperature increase induces a reduction of the intensity near the center of the distribution whereas the large tails remain unchanged. The integral intensity below a Lorentzian, however, is mainly determined by the tails of the distribution especially in a two-dimensional integration.

V. DISCUSSION

The present experiment yields the following results. The diffuse scattering above T_c exhibits an Ornstein-Zernike mean-field behavior. With increasing temperature, the long-range correlations are reduced but short-range order is present up to the melting point. The order correlations of the SCN molecules are anisotropic and are of shorter range along the tetragonal c direction. This anisotropy is conserved within the entire temperature range above T_c. Moreover, the integral intensity below the Lorentzian remains essentially constant. This means that a completely disordered structure, i.e., a random head-tail orientation of the linear SCN molecules, does not occur. The constant integral intensity near the superlattice points indicates that most of the SCN molecules are in an ordered local configuration even above the critical temperature.

On the other hand, below T_c (i.e., up to 2° below the critical temperature) no critical scattering was observed. The broad Gaussian intensity distribution at the bottom of the (100) superlattice reflection remained constant in width in a temperature range of about 20° below the transition point. This Gaussian distribution is also anisotropic in reciprocal space with, however, a much smaller anisotropy ratio as that observed above T_c for the critical scattering. The appearance of the broad diffuse intensity distribution near the superlattice points indicates the formation of small ordered clusters within the long-range-ordered orthorhombic phase. From the width of the intensity distribution, an average cluster size of about 5 lattice spacings can be evaluated.

In view of these results, the phase transition in KSCN can be described by a transformation from a long-range- to a short-range-ordered state, where most of the SCN molecules remain in a local ordered configuration.

The short-range-ordered state may be described by an ensemble of ordered domains. The number of SCN molecules which are in a disordered configuration is then given by the number of molecules near domain boundaries and is therefore proportional to the total domain interface. On the other hand, the number of SCN molecules within an ordered configuration is proportional to the volume of the domains and therefore to the volume of the crystal. If this is the case, the integral intensity in the vicinity of the superlattice points should show no important changes with temperature, as indeed observed. The "disordered" SCN molecules therefore seem to be restricted to domain boundaries and with increasing temperature the boundary density increases inducing a reduction of the correlation length between ordered SCN molecules.

Moreover, from the anisotropy of the diffuse pattern, it follows that the mean domain shape is anisotropic with a smaller size along the tetragonal direction. The anisotropic domain size and the therewith connected higher density of boundaries along the tetragonal c direction indicates a lower interfacial energy for boundaries lying in the basal plane. This last feature may be related to the elastic anisotropy of the KSCN system, i.e., the tetragonal direction is a soft elastic direction as borne out by the ratio of elastic constants $C_{33}/C_{11} \approx 0.75$.

Below T_c, within a temperature range of 20°, small ordered domains with a typical size of 20 Å were found to be embedded within the long-range-ordered orthorhombic matrix. On the average, these small ordered domains are in an "out-of-phase" relation with the surrounding ordered matrix. Indeed, domains with a coherent phase relation with the long-range-ordered crystal would essentially contribute to Bragg scattering at the superlattice points but would not induce a broad diffuse scattering at the bottom of the sharp superlattice peak.

These small "out-of-phase" domains are also anisotropic in shape with a smaller size along the c direction. The anisotropy, however, is drastically reduced when compared to the situation above T_c. The reduced anisotropy may be due to the small size of these domains and to the corresponding high curvature of the boundary stabilizing rather a spherical domain shape.

Furthermore, below T_c, a distortion scattering is observed near (002) and (004) fundamental reflections. If it is reasonably assumed that, in the domain wall the lattice constant is somewhat increased, then the ordered domains of finite size observed in the same temperature range should induce a lattice distortion of the crystal.[7] This distortion should be most pronounced along the soft tetragonal direction as experimentally observed. Above T_c, however, where the long-range order disappears and therefore the domain-wall density drastically increases, the domain walls become interconnected and consequently form an infinite percolated network.[10] In this interconnected domain-wall state, the distortion scattering disappears.[7]

Moreover, in addition to the lattice distortion, the formation of finite domains below the critical temperature should also induce a lattice expansion mediated by the long-range distortion field of the closed domain boundaries. An anomalous high lattice expansion especially along the c direction is observed below the critical temperature.[1]

The description of the short-range-ordered state by an ensemble of domains therefore is able to explain the experimental results. The correlations of longer range are reduced at higher temperatures where the domain-wall density is increased. The easy mobility of domain walls further explains the quick rearrangement of the short-range-ordered state after temperature changes, i.e., at temperatures above T_c, any variation and even accidental fluctuation of temperature is followed instantaneously by a concomitant change of diffuse intensity. The intensity behavior is also reversible with temperature. This "elastic" response of intensity to temperature changes corroborates the domain wall structure of the short-range-ordered state. Furthermore, the present experiment gives no evidence for dynamical disorder, i.e., no quasielastic broadening is connected with the elastic intensity decrease at the superlattice point. This means that a dynamical head-tail flipping of the SCN molecule is not observed in the quasielastic frequency range. This last finding is also in accordance with the present static description of the structural state above T_c where most of the SCN molecules remain within an ordered local arrangement and disorder is restricted to domain boundaries.

In summary, we have found that in KSCN orientational short-range-order of the SCN molecules is present up to the melting point. In view of the essentially constant integral short-range-order intensity above T_c, the SCN molecules are locally within an ordered configuration. The short-range-ordered state may therefore be described by an ensemble of ordered microdomains.

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