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MÖSSBAUER GAMMA-RAY DIFFRACTION FROM THE MOLECULAR CRYSTAL KCN

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Mössbauer gamma-ray diffraction was applied to separate the elastic and inelastic scattering intensities from the (200), (400) and (600) Bragg reflections of KCN. The energy resolution of our experiment was 60 neV. The Debye–Waller factor extracted from the elastic data and the thermal diffuse inelastic data both increase towards phase transiton, theoretically a logarithmic singularity was predicted.

1. INTRODUCTION

THE EXTREMELY high energy resolution of gamma-rays from a ^{57}Co-source has been utilized for a separation of elastic and inelastic components from the scattering in KCN. KCN is a simple molecular crystal with a pseudocubic sodium chloride structure at room temperature. The CN^--molecular ions are statistically distributed with probability maxima of their orientation along the {111} symmetry equivalent directions [1]. In particular inelastic neutron scattering [2–5], Raman scattering of light [6], ultrasound experiments and Brillouin scattering of light [7–9] have been applied by several groups to investigate the lattice dynamics of this crystal. As a common feature it has been pointed out that the lowest rotational excitations of the CN^--dumbells overlap energetically with the ordinary "translational phonon" modes. Actually the possibility of rotational, librational and tunneling transitions have been considered. Their influence – although not specified in single resonances – is evident as an increased "diffuse" background in the scattering experiements [2–5, 10].

The aim of our investigation was a separation of elastic and inelastic scattering intensities from KCN by means of Mössbauer gamma-ray diffraction from a single crystal. Such a separation may be interesting below Bragg peaks, because the ordinary thermal diffuse scattering (TDS) associated with the acoustic phonon branches must be sensitive to the softening of the elastic constant C_{44}, when the phase transition at $T_0 = 168$ K is approached. Since C_{44} determines the dynamics of transverse acoustic branches in a two-dimensional subspace of phonon wavevectors, KCN is one of the rare examples to study logarithmic singularities of the Debye–Waller factor and the TDS as proposed in a recent paper by Folk *et al.* [11]. A second point of interest are in the regions of enhanced "diffuse" scattering inside the Brillouin zone that have been seen in recent neutron scattering experiments [12].

2. EXPERIMENTS

The Mössbauer gamma-ray diffraction method we use has been explained in detail in previous papers [13–15]; therefore we give here only a short description of our set-up. The recoilless radiation from a 200 mCi ^{57}Co-source in a Rh-matrix was scattered from a KCN single crystal and then analysed by a black absorber of ammonium lithium fluoferrate acting as a resonance filter with an energy resolution of $dE = 60$ neV. The radiation was detected by a 80 mm^2 Si(Li) detector whose resolution is 300 eV at 14 keV. The crystal of KCN was cut with a (200) surface plane and kept in a vacuum scattering chamber during the experiment. The active area was 12 × 11 mm^2, the thickness 2 mm. The mosaic spread was less than 0.2 degree. The crystal was cooled using a closed cycle helium refrigerator, the temperature was controlled to ± 0.5 K.

In our experiment we have investigated the (200), (400) and (600) reflections of KCN with 2θ-, ω- and $(2\theta - \omega)$-scans cutting the Bragg peaks and the TDS-part along different paths in reciprocal space. In order to give an impression of the dramatic change of the thermal diffuse scattering, we present in Fig. 1 a 2θ-scan of the (200) reflection taken at 300 K and at 180 K. Since there is only a moderate change in the elastic intensity – due to the anomalous Debye–Waller factor discussed below – and a slight shift in the peak position – due to lattice constant change – we

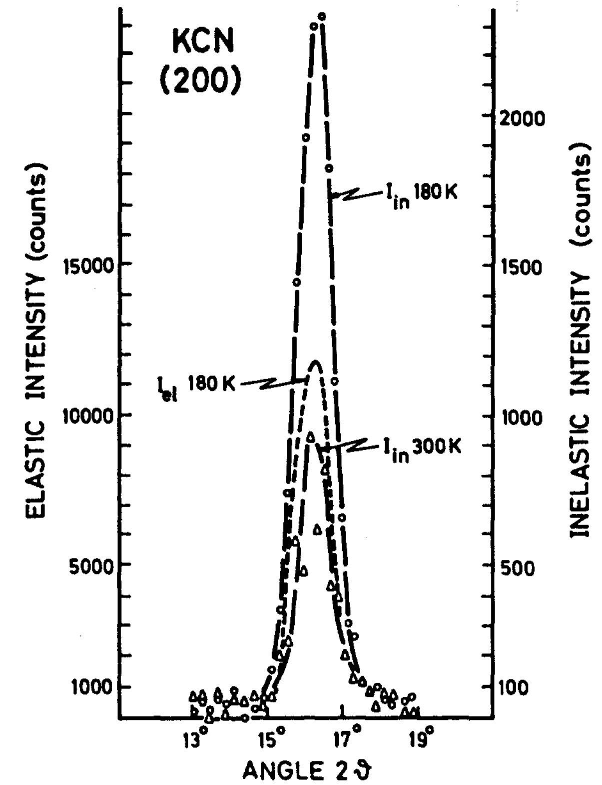

Fig. 1. Elastic and inelastic intensities from the (200) Bragg reflection of KCN. 2θ-scans at 300 K and 180 K are shown. The lines are guide for the eyes. Elastic data points are left for clarity.

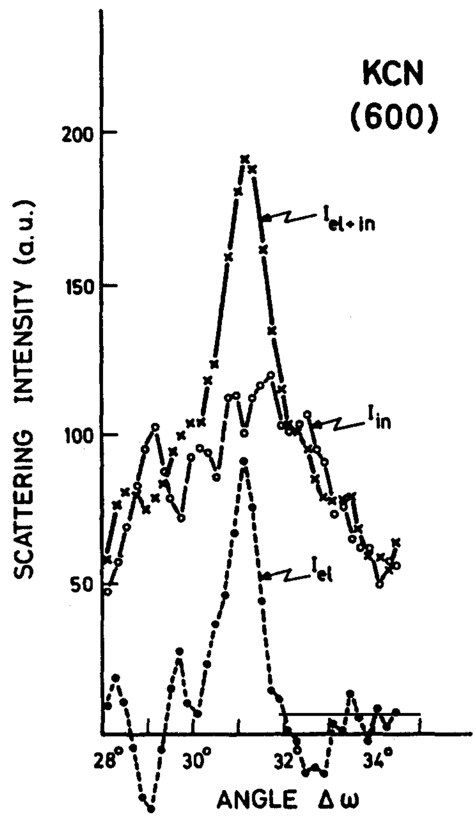

Fig. 2. Elastic, inelastic and total intensity from the (600) Bragg reflection of KCN. An ω-scan at 170 K is shown.

have left the elastic scan at 300 K for clarity. Besides the drastic intensity change of the inelastic parts we also recognize that the line width does not broaden anomalously in this scan. This may be a consequence of the rather flat four-dimensional resolution ellipsoid with $dq_x \cong 0.05 q_{max}$ and $dq_y = dq_z \cong 0.2 q_{max}$; thus its full width is about 1/10 of the diameter $2q_{max}$ of the Brioullin zone, its energy width in the fourth dimension is completely negligible due to the use of Mössbauer gamma-radiation.

It turned out that the ω-scan showed rather braod inelastic peaks due to the enhanced cross-section for the transverse modes in our scattering geometry. We demonstrate this in Fig. 2 showing an ω-scan from (600) taken at 170 K. This experiment also shows that the inelastic intensity is larger in magnetude than the elastic part. Consequently there is a large TDS correction necessary to extract the elastic scattering intensities which are relevant for a determination of the probability distribution of CN^--dumbbells that have been reported in the literature [1]. We conclude that it seems to be necessary to repeat these diffraction experiments with high energy resolution guaranteeing a sophisticated TDS correction.

The temperature dependence of the elastic and inelastic intensities taken at the peak maximum of the (200) reflection are shown in Fig. 3. Here again we realize the drastic increase of the inelastic part which fits to some extent to a logarithmic law predicted theoretically [11]. Such a logarithmic singularity is expected for the inelastic cross-section involving the dynamic susceptibility integrated over the resolution ellipsoid.

$$I_{in} \propto \sum_q \int_{(1/\hbar)dE}^{\infty} d\omega \frac{kT}{\hbar\omega} \operatorname{Im} \chi(q, \omega).$$

The elastic part of the scattering shown in Fig. 3 is almost constant in the investigated temperature range which is unusual also. Normally one expects the elastic scattering to decrease with rising temperature due to the Debye–Waller factor. Thus our data indicate an anomalous Debye–Waller factor. We can extract from our elastic date an overall Debye–Waller factor $W(T)$ using the following relation.

$$W(T) = W(300) - 0.5 \ln \left[\frac{I(T)}{I(300)}\right].$$

The room temperature value, we took from [16], $W(300) = 4.85 \sin^2\theta/\lambda^2$ is comparable to the value given

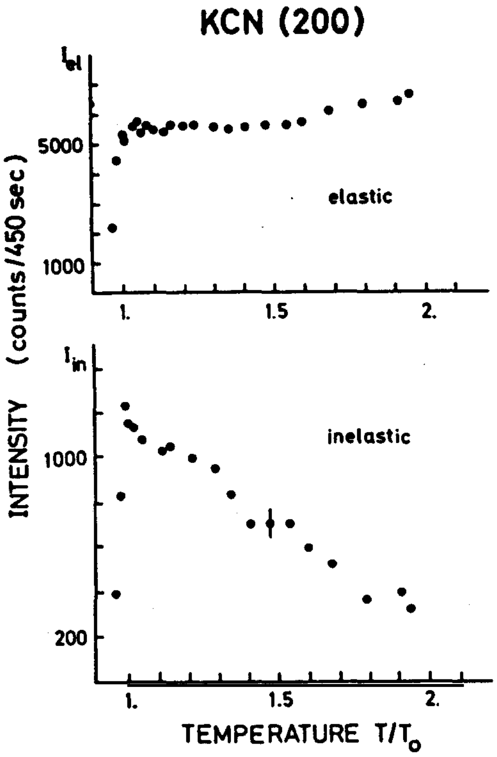

Fig. 3. Temperature dependence of the elastic and inelastic intensity taken at the peak maximum of the (200) reflection of KCN.

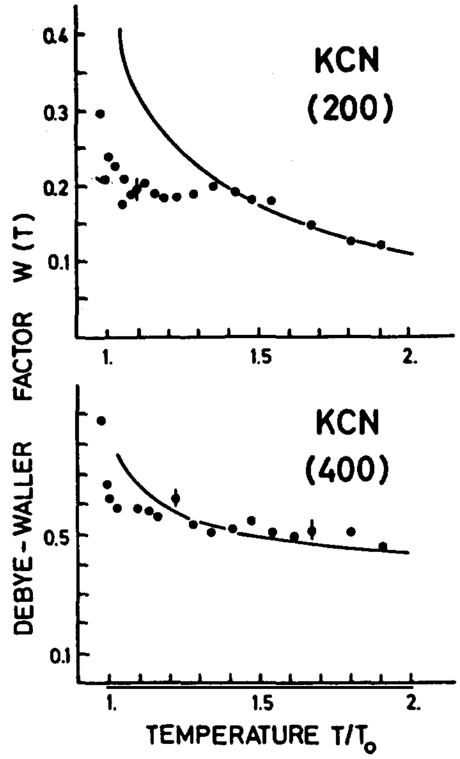

Fig. 4. Debye–Waller factor $W(T)$ at the (200) and (400) Bragg reflections of KCN. Full lines represent the law $W(T) = a(\sin^2\theta/\lambda^2) + b|\ln\tau|$ with $a = 4.42$ A^2 and $b = 0.10$.

in [1]. The data extracted from the (200) and (400) elastic intensities are plotted in Fig. 4. The experimental points which increase towards the phase transition temperature are compared with a theoretical curve consisting of a normal part and a logarithmic correction.

$$W(T) = a\,\frac{\sin^2\theta}{\lambda^2} + b|\ln\tau|; \quad \tau = \frac{T-T_0}{T_0}.$$

Note that the constants a and b are determined at one momentum transfer $Q^2 \sim \sin^2\theta/\lambda^2$ only.

We recall that the phase transition in KCN at $T_0 = 168$ K is a first order one because of nonvanishing third order invariants to the elastic energy. Logarithmically diverging local fluctuations would also support the first order character of a phase transition [11]. Thus we conclude that the transition in KCN is almost second order which is seen from the tendency of logarithmically diverging Debye–Waller factors and thermal diffuse scattering; deviations are evident near T_0 which may be the consequence of the actual first order character.

In order to determine the nature of the coupling of CN^--dumbbells we have also investigated the Brillouin zone boundary at the X-point of the pseudo-cubic high temperature phase with the Mössbauer gamma-ray diffractometer. This was done in 2θ–ω scans along the line (200) to (600) in reciprocal space. We find in this experiment increased inelastic intensity which surmounts the elastic part by a factor of two and seems to peak at the X-point. From neutron experiments [12] one expects a flat and broad branch of molecular excitations with a weak temperature dependent softening at the zone boundary. Ultrasonic results [17] indicate an anti-ferrodistortive ordering, which would be more likely to fit the present experiments.

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