Critical scattering of x rays in potassium dihydrophosphate (KDP)

A. N. Zisman
Institute of Crystallography, Academy of Sciences of the USSR

(Submitted 24 July 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 6, 354–357 (20 September 1981)

The diffuse scattering of x rays in the neighborhood of the tricritical point on the structural phase-transition line is analyzed for the first time. The values of the index ν, which characterizes the behavior of the correlation radius $\nu' = 0.23 \pm 0.05$ for the weakly symmetric phase and $\nu = 0.43 \pm 0.1$ for the strongly symmetric phase, are determined.

PACS numbers: 78.70.Ck, 64.70.Kb, 64.60.Fr, 61.60. + m

In our x-ray studies of the order parameter in KDP in the neighborhood of the tricritical point, we have encountered an anomalous increase in intensity of the diffracted beam [(200) reflection] in the immediate vicinity of the phase transition ($|T-T_c| \sim 0.1$ K). An increase in diffuse scattering in the neighborhood of the phase transition, which was described by Landau for the first time,[1] gives the most reasonable explanation of this effect. It is known that diffuse scattering provides the information on the behavior of the correlation radius of fluctuations in the neighborhood of the phase transition. Unfortunately, the instrumentation used by us in the experiment could not reliably separate the coherent component from the incoherent component of the diffracted beam, a function necessary to obtain quantitative information on diffuse scattering.

These circumstances stimulated us to conduct this study, whose aim is to analyze the diffuse scattering quantitatively in the neighborhood of the tricritical point on the ferroelectric phase-transition line in KDP.[1)]

The geometry of the experiment is illustrated in Fig. 1. The x-ray beam from a molybdenum anode, after a Bragg (111) reflection by a monochromator crystal 1 prepared from a perfect silicon single crystal, was transmitted through a collimator 2, in which the $K_{\alpha 1}$ line was separated out. The beam produced in this manner was directed to the crystal 3 to be analyzed, in which it was reflected to produce a Laue diffraction pattern. The beam scattered by the sample, after a Bragg (111) reflection by a germanium analyzer-crystal 4, was recorded by a scintillation counter 5. All three crystals were mounted on the GUR-5 goniometer. The sample with dimensions $1 \times 1 \times 5$ mm along the X, Y, Z axes, respectively (the Z axis is perpendicular to the drawing plane) was placed into a high-pressure cell. The cell temperature was stabilized to an accuracy of ±0.2 mK, and the pressure was maintained with an accuracy of ±0.2 bar. The crystal under investigation was part of a single crystal that was analyzed previously by using a dilatometric method,[2] for which the coordinates of the tricritical point have been established, $P = 2640 \pm 40$ bar, $T = 109.8 \pm 0.2$ K. The Bragg angles for the (111) reflection of the analyzer and monochromator and for the

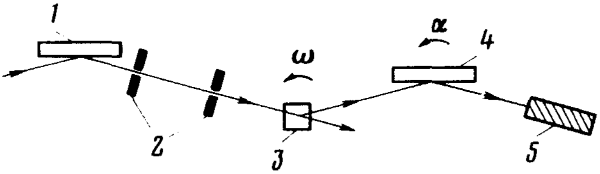

FIG. 1. Experimental arrangement.

(200) reflection of the KDP crystal are very close in magnitude. This enabled us to obtain narrow (~8″), coherent diffraction peaks despite rather large angular divergence (~1′) of the incident beam.[3] If the reflecting planes of all three crystals are parallel, the intensity of the x-ray beam recorded by the detector is determined by the sum of the diffuse and diffracted components. If, however, the sample is rotated by a small angle ω with respect to the Z axis ($\omega \gtrsim 30$), then the analyzer crystal will reflect into the detector only the diffuse component, and in order to record the coherent component, we must turn the crystal through an angle $\alpha \approx \omega$, which is determined by the continuity condition of the tangential part of the coherent component at the boundary of the analyzed crystal.[3,4] Figure 2 shows the intensity plotted as a function of the angle of rotation of the crystal for $\omega \approx 30''$. Thus, after initially placing all three crystals in the reflecting position and plotting the distribution of the intensity $I(\omega)$ in the region $\omega \geqslant 30''$, we obtained a dependence of the diffuse component $I(g)$ for the $\mathbf{q}$ vectors which lie in the (XY) plane and which are perpendicular to the reciprocal-lattice vector $\mathbf{K}$ for the (200) reflection. The $\mathbf{q}$ vector is related to ω by the relation

$$|\mathbf{q}| \approx |\mathbf{K}|\,|\sin\omega| \approx |\mathbf{K}|\,|\omega|\,. \qquad (1)$$

It was established[5] that, because of the piezoelectric effect in the nonpolar phase, only those fluctuations $\Delta\eta$ in KDP crystals are critical whose wave vector is in the (XY) plane and is parallel to either the X or the Y crystallographic axis. Thus it follows from our discussion that ω scanning of the region surrounding the (200) reciprocal lattice site reveals that scattering occurs during critical fluctuations. These

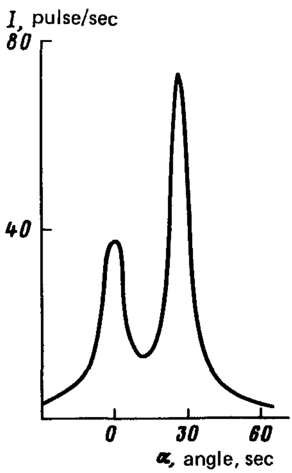

FIG. 2. Dependence of the intensity I on the angle of rotation α of the analyzer for $\omega \approx 30''$.

fluctuations produce a transverse strain wave in KDP crystals, which is the main source of diffuse scattering. According to Ref. 6, the intensity of the diffuse component under these conditions can be written as follows:

$$I(\mathbf{q}) \sim \frac{|\mathbf{K}|^2}{|\mathbf{q}|^2} \overline{|\Delta\eta(\mathbf{q})|^2}. \tag{2}$$

The expression for critical fluctuations, for the condition $\mathbf{q} \parallel \mathbf{e}_x$ or $\mathbf{q} \parallel \mathbf{e}_y$, can be written in the form

$$\overline{|\Delta\eta(q)|^2} \sim \frac{r_c^2(\tau)\, T}{1 + r_c^2(\tau)\, g^2/2}, \tag{3}$$

where $\tau = (T - T_c)/T_c$, and r_c is the correlation radius. Substituting Eqs. (1) and (3) in Eq. (2), we obtain a definitive expression for the intensity of diffuse scattering I, as a function of the angle ω and temperature T,

$$I(\omega, T) = \frac{I_0(T)}{1 + r_c^2 K^2 \omega^2/2}, \tag{4}$$

where

$$I_0(T) = \text{const}\; T r_c^2(\tau).$$

A statistical analysis of the experimental dependences $I(\omega)$ obtained at a pressure $P = 2637.5$ bar at different temperatures within the range of angles $\omega \epsilon (-0.2^\circ; +0.2^\circ)$ showed that they are described adequately by the expression (4). The most accurate quantity determined by this analysis is $I_0(T)$, which is proportional, according to Eq. (4), to the square of the correlation radius. The obtained $I_0(T)$ dependence in the immediate vicinity of the transition is shown in Fig. 3. In

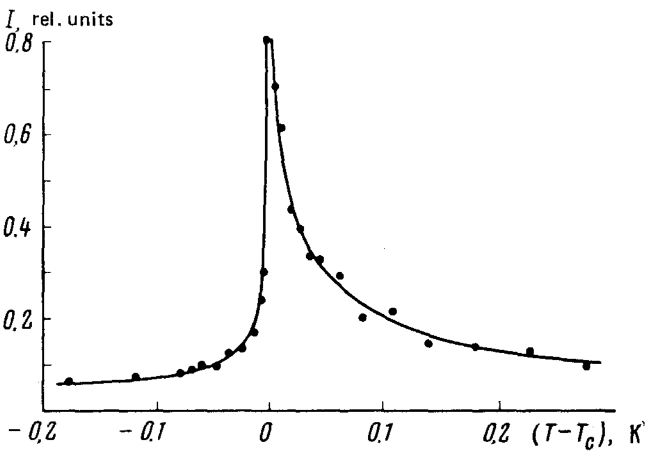

FIG. 3. Experimental dependence of I_0 on temperature at $P = 2637.5$ bar.

the neighborhood of the phase transition the correlation radius r_c is described by the expression $r_c \sim |\tau|^{-\nu}$. The statistical analysis of the experimental dependence $I_0(T)$ and the search for the values of the index ν and the transition temperature T_c gave the value $\nu = 0.43 \pm 0.1$ for $T > T_c$ and $\nu' = 0.23 \pm 0.05$ for the region $T < T_c$ at the 95% probability level. This result is in good agreement with the conclusions of the theoretical studies.[5,7,8] According to these studies, because of nonzero shear modulus, the correlation radius for the ordered phase is described by the index $\nu' = \beta$ (the index of the order parameter β is equal to 0.25) in the neighborhood of the tricritical point on the structural phase-transition line. At the same time, $\nu = 0.5$ for the disordered phase.

In conclusion, the author would like to take this opportunity to thank S. M. Stishov, V. M. Kaganer, É. K. Kov'ev, and I. V. Aleksandrov for their constant interest and cooperation, and also A. P. Levanyuk, S. A. Minyukov, and D. E. Khmel'nitskiĭ for a discussion of the results.

[1)]Until now, we have not found in the literature any reference to a quantitative analysis of diffuse scattering or the behavior of the correlation radius in the neighborhood of the tricritical point on the structural phase-transition line.

1. L. D. Landau, Zh. Eksp. Teor. Fiz. 7, 1232 (1937).
2. A. N. Zisman, V. N. Kachinskiĭ, and S. M. Stitov, Pis'ma Zh. Eksp. Teor. Fiz. **31**, 172 (1980) [JETP Lett. **31**, 158 (1980)].
3. Z. G. Pinsker, Dinamicheskoe rasseyanie rentgenovskikh lucheĭ v ideal'nykh kristallakh (Dynamic Scattering of X Rays in Ideal Crystals), Nauka, Moscow, 1974.
4. A. Iida and K. Kohra, Phys. Stat. Sol. (a) **51**, 533 (1979).
5. A. P. Levanyuk and A. A. Sobyanin, Pis'ma Zh. Eksp. Teor. Fiz. **11**, 540 (1970) [JETP Lett. **11**, 371 (1970)].
6. M. A. Krivoglaz, Teoriya rasseyaniya rentgenovskikh lucheĭ i teplovykh neĭtronov real'nymi kristallami (Theory of X-Ray and Thermal-Neutron Scattering by Real Crystals), Nauka, Moscow, 1967.
7. V. L. Ginzburg and A. P. Levanyuk, Phys. Lett. Ser. A **47**, 345 (1974).
8. A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **66**, 2255 (1974) [Sov. Phys. JETP **39**, 1111 (1974)].

Translated by S. J. Amoretty

Edited by Robert T. Beyer