STRUCTURAL CHANGES IN QUARTZ DURING THE $\alpha \to \beta$ TRANSITION

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STRUCTURAL CHANGES IN QUARTZ DURING THE $\alpha \to \beta$ TRANSITION

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After a certain degree of neutron irradiation, the structure of some crystals acquires features characteristic of high-temperature modifications ([1−3]). On the basis of the literature data ([2]) and of data obtained by us ([3]), it may be supposed that, under irradiation, the transition from one modification to another is effected through displacements of atoms; moreover, the decisive role is played by the type of structure and by the number of displaced atoms. In this respect, the study of structural temperature transformations becomes of particular interest, especially if one takes into account that transitions in structures of a definite type ("subcritical" and "critical," in Semenenko' s terminology ([4])) are observed over a fairly wide temperature interval ([5]).

The purpose of the present work is to follow the changes in the structure of α-quartz upon heating. As the principal method of investigation we used the diffuse-scattering method, based, as is known, on the scattering of x-rays by atoms displaced from positions of stable equilibrium. In parallel, x-ray photography was carried out by the Laue method.

Noticeable changes in the ratio of the intensities of the Laue maxima are observed already at a temperature of 100° (Fig. 1a). Against the background of a monotonic decrease in intensity, characteristic in the temperature interval 20–540° for most reflections, including reflections of the type $(0\bar{3}31)$—$[(I_T - I_{T=20^\circ})/I_{T=20^\circ}]_{\text{av}}$—the behavior of reflections of three types stands out: $(5\bar{3}83)$, $(\bar{3}3\bar{6}2)$, and especially $(30\bar{3}1)$ (Fig. 1a). $I_{30\bar{3}1}$ first decreases noticeably (in the interval from 20 to 260°), at a temperature of approximately 460° is restored, and with a further increase in temperature begins to increase—at first slowly, and then ever more sharply as the transition temperature is approached ($T_{\alpha\to\beta} = 576^\circ$). It should be noted that in the interval 540–580° a noticeable change in intensity is observed for many reflections—an increase or a decrease; moreover, as for reflections of the type $(30\bar{3}1)$, this change is at first weakly expressed, and then, on approaching the temperature $T_{\alpha\to\beta}$, the rate of change increases sharply (Fig. 1b). A further increase in temperature from 580 to 800° does not substantially change the intensity ratio attained at $T_{\alpha\to\beta}$. Only a general decrease in intensity is observed, proceeding just as

Fig. 1. Character of the change in the intensity of Laue maxima as a function of temperature. a $-(I_T - I_{T=20^\circ})/I_{T=20^\circ}$; b $-I_T$

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slowly and smoothly as was observed for most reflections in the interval from 20 to 540°. It may only be noted that, for some reflections, this decrease is larger in magnitude in the interval from 600 to 700°.

When monochromatic radiation is used, noticeable changes in the scattering of x-rays appear at a temperature of about 300°. This is manifested first of all in an increase in the sharpness of the nonradial streaks connecting the diffuse maxima, as a result of which the shape of the diffuse maxima also changes. With an increase in temperature to 380°, this becomes so pronounced that the overall intensity distribution becomes, as it were, intermediate between the scattering of α- and β-quartz, but more similar to that characteristic of β-quartz (Fig. 2). How-

···the principal features of α-quartz: the difference in geometry and, correspondingly, in the intensities of diffuse scattering at nodes of the type $(30\bar{3}1)$ and $(03\bar{3}1)$ at this temperature are still clearly noticeable. The equalization of intensity and the achievement of correspondence in the positions of the diffuse maxima occur because the pattern of diffuse scattering at the nodes $(30\bar{3}1)$ is mainly rearranged. This change takes place very smoothly (Fig. 3) and over a very broad temperature interval—of the order of 200° (from 380 to $580 \pm 5^\circ$). It is true that after 500° this process proceeds more actively. In the same temperature interval there is also observed a more subtle

Fig. 1. Character of the change in the intensity of Laue maxima as a function of temperature.
a $-(I_T - I_{T=20^\circ})/I_{T=20^\circ}$; *b* $-I_T$

phenomenon—the change in the shape of the diffuse maxima, not connected with the previously noted increase in the sharpness of the nonradial streaks. This change in shape does not end upon reaching $T_{\alpha\to\beta}$. Likewise, complete identity in the distribution of the diffuse-scattering intensity in accordance with the symmetry C_6 is not observed at $T_{\alpha\to\beta}$ (Figs. 2 and 3), but is achieved at higher temperatures—of the order of 700–750°.

The data obtained clearly show that the $\alpha \to \beta$ transition occurs very smoothly and over a sufficiently broad temperature interval. Moreover, the rearrangement is carried out, as it were, in three stages: I—the preparation for rearrangement (from 300° or less to 540–560°) according to the data of the diffuse-scattering method and the Laue method; II—the rearrangement proper (from 540–560 to $580 \pm 5^\circ$) according to the Lauegrams; III—the adjustment (from 580 to 700°) according to the data of the Laue method and diffuse scattering, since from the change in the shape of the diffuse maxima there unambiguously follows a change

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

in the complete spectrum of atomic vibrations.

It is characteristic that the diffuse scattering of X-rays over the entire temperature interval from 300 to 700–750° changes very smoothly. This applies both to the increase in the sharpness of the nonradial streaks, and to the change in the shape of the maxima, and to the geometry of their arrangement, and to the equalization of the intensities in accordance with the symmetry C_6. Consequently, one may conclude that the displacement of atoms from the old equilibrium positions into new ones does not occur discontinuously upon reaching $T_{\alpha\to\beta}$, but smoothly as the temperature rises. At different stages only the magnitude of the displacement changes, and the atomic displacements are, as it were, directed by the fields of interatomic interaction. This conclusion follows from the change in the intensities of the various Laue and diffuse maxima as the temperature is increased.

Fig. 2. X-ray diffraction patterns obtained with monochromatic K_αMo radiation. The beam is parallel to the [001] direction. *a*—380°, *b*—580°

Fig. 3. Diffuse scattering at nodes of the type $(30\bar{3}1)$ and $(03\bar{3}1)$: *A*—regions of the X-ray diffraction patterns, *B*—schematic representation. 2×. *a*—T_k, *b*—480°, *c*—580°, *d*—750°, *e*—T_k

Thus, the temperature transition $\alpha \to \beta$ is very close to those structural changes that are observed in quartz under neutron irradiation from 10^{19} to $5\text{-}6 \cdot 10^{19}$ n/cm^2, and to each temperature interval one may assign a corresponding interval of values of the integral flux*. At the same time it is necessary to limit both the temperature (approximately up to 700°) and the value of the integral flux (up to $5\text{-}6 \cdot 10^{19}$ n/cm^2), since the structure obtained under further irradiation (of the order of $7 \cdot 10^{19}$ n/cm^2) resembles neither β-quartz nor tridymite ([3]).

The experimental data we have obtained do not contradict the change in structure-sensitive properties observed during the $\alpha \to \beta$ transition in quartz, although on the basis of these data $T_{\alpha\to\beta}$ is determined quite clearly. In our opinion, the principal role here is played by the sensitivity of a given method to the character of the change in the magnitude of atomic displacements. At the first stage (300–540°) the atomic displacements, although they change in magnitude, change slowly, and the properties accordingly change slowly and smoothly ([7]). Beginning at temperatures of 550–560°, an increase in the displacement magnitudes is observed, which is also marked by the appearance of λ-peaks on the curves of the dependence of elastic characteristics, heat capacity, thermal expansion, molecular light scattering, etc., on temperature ([8-11]). Those properties that are sensitive to maximal changes in the positions of atoms are characterized by a kink or inflection near $T_{\alpha \to \beta}$ ([12]). In the region of "completion" (580–700°) only those properties change that depend on the subtleties in the structure of the complete spectrum of atomic vibrations, for example, elastic characteristics ([7,8]).

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* This conclusion is in qualitative, but not quantitative, agreement with work ([6]).

Note: Figure translations are in progress. See original paper for figures.