$$\alpha_4 = C_{44} - \frac{F_2^2}{\alpha_2} - \frac{C_{14}^2}{\alpha_1} - \frac{F_3^2}{\alpha_3}$$

where

$$F_1 = C_{23} - \frac{C_{12}C_{13}}{C_{11}}$$

$$F_2 = C_{24} - \frac{C_{12}C_{14}}{C_{11}}$$

$$F_3 = C_{34} - \frac{F_1F_2}{\alpha_2} - \frac{C_{14}C_{13}}{\alpha_1}.$$

$$G + iH = -i\mu \sum_{i=1}^{4} \sum_{j=1}^{4} X_i^0 B_{ij} X_j^0 + \frac{D_1^2}{\alpha_1} + \frac{D_2^2}{\alpha_2} + \frac{D_3^2}{\alpha_3} + \frac{D_4^2}{\alpha_4}$$

where

$$D_1 = i\mu \sum_{i=1}^{4} B_{1i} X_i^0$$

$$D_2 = \frac{C_{12}D_1}{C_{11}} - i\mu \sum_{i=1}^{4} B_{2i} X_i^0$$

$$D_3 = \frac{C_{13}D_1}{C_{11}} - \frac{F_1D_2}{\alpha_2} - i\mu \sum_{i=1}^{4} B_{3i} X_i^0$$

$$D_4 = \frac{C_{14}D_1}{\alpha_1} - \frac{F_2D_2}{\alpha_2} - \frac{F_3D_3}{\alpha_3} - i\mu \sum_{i=1}^{4} B_{4i} X_i^0.$$

The addition of a term linear in ω allows a parabolic dispersion surface, as found for example in a ferromagnet, to be treated. A constant term in the equation of the dispersion surface allows an energy gap at $\mathbf{Q}=0$. The result of these additions are further terms in equation (A1) which becomes

$$I(\mathbf{X}^0) = \int \exp -\left\{ \sum_{i=1}^{4} \sum_{j=1}^{4} [X_i A_{ij} X_j + i\mu(X_i^0 + X_i) B_{ij} (X_j^0 + X_j)] + i\mu(T(X_4^0 + X_4) + H) \right\} \prod_{i=1}^{4} \mathrm{d}X_i \tag{A4}$$

where T and H are constant coefficients.

The result of these integrations is again of the form of equation (A2) and the values of E and F are as before except that

$$D_4 = \frac{C_{14}D_1}{\alpha_1} - \frac{F_2D_2}{\alpha_2} - \frac{F_3D_3}{\alpha_3} - i\mu \sum_{i=1}^{4} B_{4i} X_i^0 - i\mu T$$

and

$$G + iH = -i\mu \sum_{i=1}^{4} X_i^0 B_{ij} X_j^0 + \frac{D_1^2}{\alpha_1} + \frac{D_2^2}{\alpha_2} + \frac{D_3^2}{\alpha_3} + \frac{D_4^2}{\alpha_4} - i\mu(H + T\omega_0).$$

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Neutron Diffraction Effects due to the Lattice Displacement of a Vibrating Quartz Single Crystal

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The time modulation of neutrons diffracted by a quartz single crystal is investigated. The experimental results agree with the aberration and with the Doppler effect caused during neutron diffraction by vibrations of a single crystal.

Introduction

In diffraction experiments, neutrons with a wavelength of $\lambda = 1$ to 2 Å are conventionally used. These neutrons with velocities of 4×10^5 to 2×10^5 cm.sec^{-1} are also suitable for the investigation of dynamical effects together with the displacement of crystallographic planes and its influence upon the process of neutron diffraction. These dynamical effects are caused by two physical processes. The first is the vector addition of neutron velocity and the velocity of lattice-plane displacement, *i.e.* the aberration effect; the second represents the relative change of neutron wavelength, *i.e.* the Doppler effect. They can be observed in the course of neutron diffraction even for small velocities of the periodic displacement of crystallographic planes with respect to the neutron velocity.

In the papers of Brockhouse (1961); Shull & Gingrich (1964); Shull, Morash & Rogers (1968) and Alefeld, Birr & Heidemann (1968), these effects were found to exist for the mechanical periodic motion of specimens having velocities of diffraction lattice planes in the range 10^3 to 10^4 cm.sec^{-1}. In the process of neutron diffraction by a vibrating quartz single crystal these effects were first observed by Michalec, Chalupa, Petržílka, Galociová, Zelenka & Tichý (1969).

Theoretical considerations

Consider a bar-shaped single crystal vibrating longitudinally in the direction of the y axis (Fig. 1). Here we can write the amplitude of the vibrating specimen in the form (Cady, 1964)

$$u = u_0 \sin \frac{\pi y}{l} \sin \omega t\,, \tag{1}$$

where u_0 is the amplitude at the ends of the bar, l is the length of the bar and $f = \omega/2\pi$ is the resonance frequency.

The velocity of the motion of crystallographic lattice planes of the bar in the direction of the y axis is then given by the relation

$$v = v_p \cos \omega t\,, \qquad v_p = u_0 \omega \sin \frac{\pi y}{l}\,. \tag{2}$$

If the diffraction lattice plane of the single crystal is moving with some velocity a change in the Bragg angle θ_B is to be expected. In the case when the direction of the velocity amplitude v_p is collinear with the reciprocal lattice vector $\boldsymbol{\tau}$, $v_p/v_n \ll 1$ expresses the change of the diffraction angle θ_B in the form

$$\delta_t = \delta_{0t} \cos \omega t \tag{3}$$

where

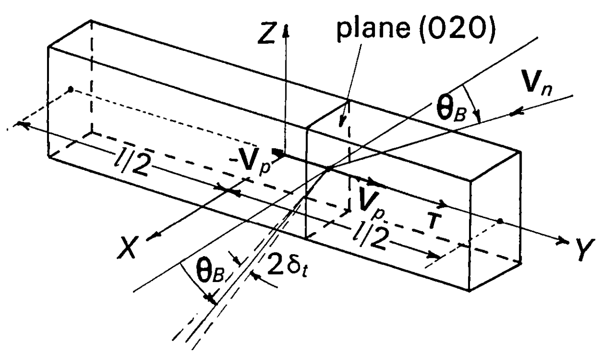


Fig. 1. Schematic arrangement for the neutron diffraction by a vibrating bar cut from a quartz single crystal with respect to the crystallographic system of coordinates in the way shown.

$$\delta_{0t} = \frac{v_p}{v_n} \cos \theta_B + \frac{v_p}{v_n} \sin \theta_B \tan \theta_B = \frac{v_p}{v_n} \frac{1}{\cos \theta_B} \tag{4}$$

which conforms with equation (1) of Shull *et al.* (1958). The first term of the equation (4) is due to aberration, the second one to the Doppler effect.

The rocking curve of the single crystal can be expressed in the form

$$J(\delta) = J(0) \exp\left(-\frac{\delta^2}{2\sigma^2}\right) \tag{5}$$

where $J(0)$ is the neutron intensity in the maximum of the rocking curve, $\delta_0 = \theta - \theta_B$ is the deviation from the Bragg angle θ_B and σ is connected with the full width w of the rocking curve at half maximum intensity by the relation

$$w = 2\sigma(2\ln 2)^{1/2}\,. \tag{6}$$

The influence of the periodic displacement of the vibrating bar on the deviation δ can be described by the relation

$$\delta = \delta_0 + \delta_t = \delta_0 + \delta_{0t} \cos \omega t \tag{7}$$

in which δ_0 is a time-independent deviation from the Bragg angle given by the position of the diffracting lattice plane and δ_{0t} is given by equation (4). The influence of the periodic time variation on δ, *i.e.* of the time modulation on the neutron intensity $J(\delta, t)$ can be described by analogy to (5) by the corresponding expression

$$J(\delta, t) = J(0, t) \exp\left[-\frac{(\delta_0 + \delta_t)^2}{2\sigma^2}\right]. \tag{8}$$

The value $J(0, t)$ represents the time modulated maximum intensity of the rocking curve in the position $\delta_0 = 0$ (Petržílka, 1968).

Applying the following relations (Jahnke, Emde & Lösch, 1960; Jeffreys & Jeffreys, 1946)

$$\exp(ix \sin \Theta) = \sum_{n=-\infty}^{+\infty} J_n(x) \exp(in\Theta)\,, \tag{9}$$

$$J_n(iz) = \exp\left(n \frac{\pi}{2} i\right) I_n(z)\,, \tag{10}$$

where $J_n(x)$ and $I_n(z)$ are Bessel functions of the nth order of the real and imaginary argument. Substituting for δ_t from equation (3), equation (8) becomes

$$J(\delta, t) = J(\delta_t, t) \exp\left(-\frac{\delta_0^2}{2\sigma^2}\right) \times \sum_{n=-\infty}^{+\infty} I_n\left(\frac{\delta_0 \cdot \delta_{0t}}{\sigma^2}\right) \exp[in(\omega t + \pi)] \tag{11}$$

where

$$J(\delta_t, t) = J(0, t) \exp\left(-\frac{\delta_{0t}^2}{4\sigma^2}\right) \times \sum_{m=-\infty}^{+\infty} I_m\left(\frac{\delta_{0t}^2}{4\sigma^2}\right) \exp[im(2\omega t + \pi)]\,. \tag{12}$$

As can be seen from equations (11) and (12), supplementary modulations occur in addition to the time modulation of diffracted neutrons. At the maximum of the rocking curve ($\delta_0=0$) the supplementary modulation components are $a_2 \cos 2\omega t$, $a_4 \cos 4\omega t$, $a_6 \cos 6\omega t$, *etc.* In positions where $\delta_0 \neq 0$ still further modulation components occur, $b_1 \cos \omega t$, $b_2 \cos 2\omega t$, $b_3 \cos 3\omega t$, *etc.*, which are due to the influence of aberration and the Doppler effect on the time modulation of neutrons diffracted by a vibrating single crystal.

Experimental results

Neutron diffraction by a vibrating quartz single crystal was investigated using the double-axis spectrometer (Michalec, Vavřín, Chalupa & Vávra, 1967). A beam of monoenergetic neutrons with wavelength $\lambda = 1{\cdot}54$ Å impinging the investigated specimen was diffracted by the plane (020) in the position of a symmetric transmission and detected by a thin [ZnS(Ag) + ^{10}B] detector. The centre of the neutron beam impinging the lattice plane was at a distance $y = 3l/8$ from the centre of the vibrating quartz bar. The time modulation of diffracted neutrons was measured by a multichannel analyzer by applying the time digital converter with the channel width of 1μs.

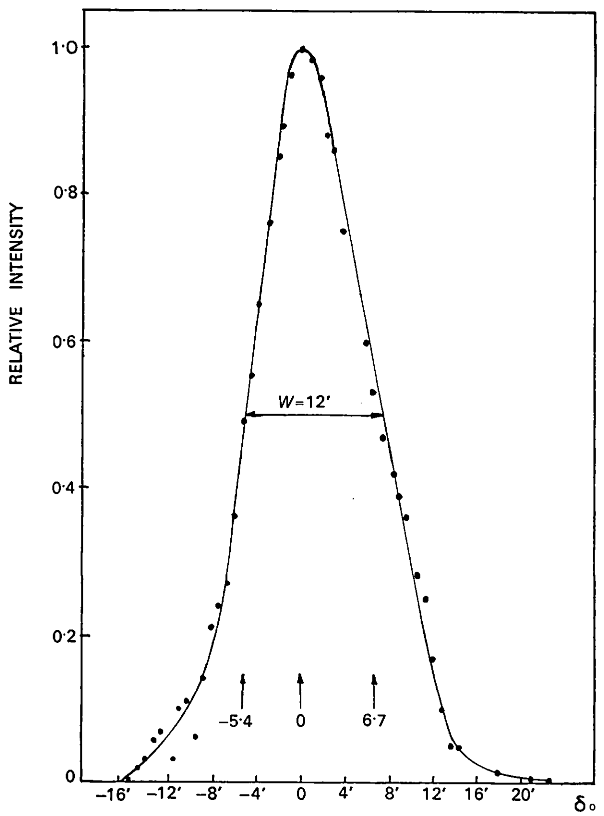


Fig. 2. Rocking curve for the (020) diffraction of the vibrating quartz single crystal. In the positions marked by arrows measurements of the time modulation of diffracted neutrons were made.

The quartz single crystal was bar shaped having dimensions of 3 mm in the X direction, 120 mm in the Y direction and 14 mm in the Z direction (Fig. 1). The bar was piezoelectrically excited in the series resonance

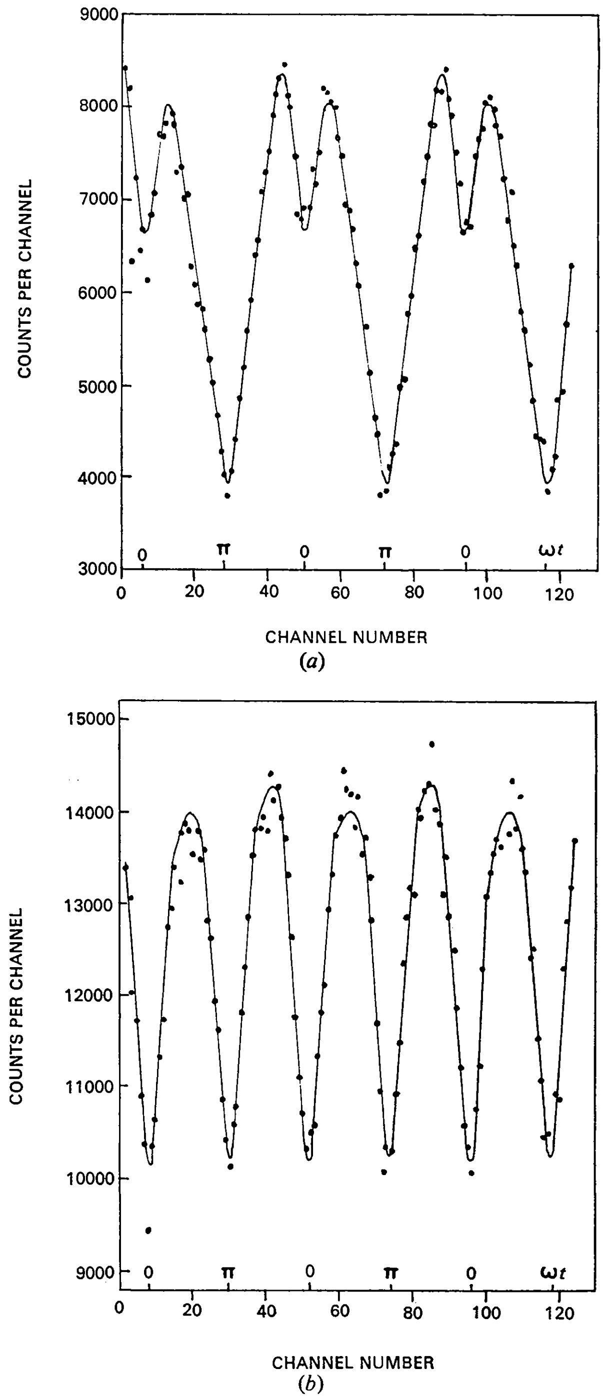
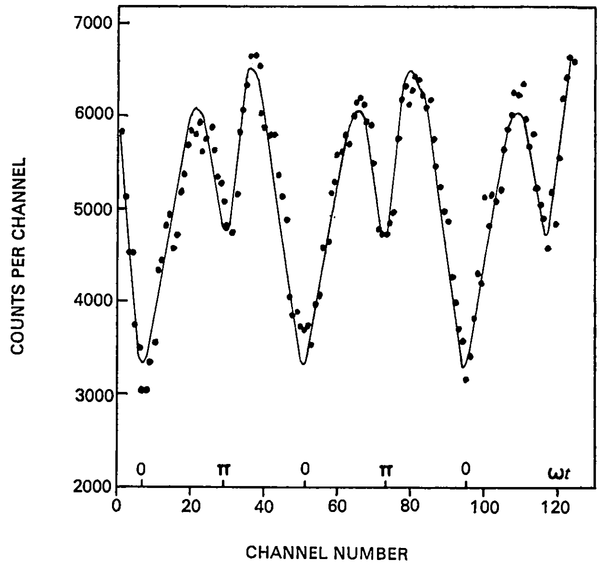


Fig. 3. Time modulation of neutrons diffracted by vibrating quartz single crystal in the position with (*a*) $\delta_0 = -5{\cdot}4'$, (*b*) $\delta_0 = 0$. The smooth curves were obtained from experimental values of neutron intensities by the method of minimum squares.



(c)

Fig. 3 (*cont.*) (*c*) $\delta_0 = +6{\cdot}7'$,

of the fundamental mode of vibration having the resonance frequency $f = 22{\cdot}6$ kHz. The high frequency current flowing across the bar was maintained constant for all measurements and equal to $i = 2{\cdot}1$ mA.

Fig. 2 shows the rocking curve of the vibrating quartz single crystal. The full width at half maximum intensity of this curve is equal to $w = 12$ min of arc. For the non-vibrating single crystal the full-width of the rocking curve in our experimental arrangement was equal to that for the vibrating crystal (Chalupa, Michalec, Petržílka, Tichy & Zelenka, 1968). The measurements of the time modulation of diffracted neutrons was performed in points marked on the rocking curve.

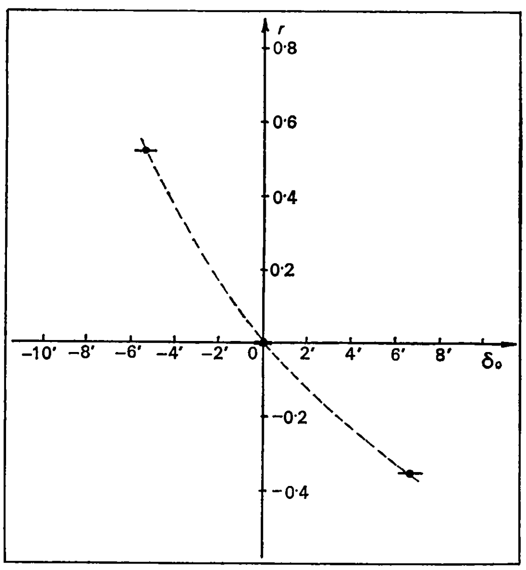


Fig. 4. Experimental values of r as a function of δ_0. The dashed line shows the relationship between r and δ_0.

Fig. 3 illustrates the measurements of the time modulation of neutrons diffracted by a vibrating single crystal in positions $\delta_0 = -5{\cdot}4'$ [Fig. 3(*a*)], $\delta_0 = 0$ [Fig. 3(*b*)] and $\delta_0 = +6{\cdot}7'$ [Fig. 3(*c*)]. The intensity of neutrons for a non-vibrating single crystal is time independent in all positions and about four times smaller than the mean intensity of neutrons diffracted by a vibrating single crystal.

Discussion

Fig. 3 shows that the curve of the time modulation of the neutron beam has a quite different course of taken at different points of the rocking curve, the position of which is characterized by the value of δ_0. This value is due to aberration and the Doppler effect on the diffraction of neutrons by a vibrating single crystal.

At the maximum of the rocking curve ($\delta_0 = 0$) it is possible to express the time modulation of neutrons by equation (12). Since all minima of the modulation curve are equal, we can write the relation

$$J(0, \omega t = 0) = J(0, \omega t = \pi)\,.$$

The time modulation of neutrons diffracted in positions with $\delta_0 \neq 0$ may be described by equation (11). The experimental data show that significant differences exist in the depth of minima, for which $\omega t = 0$ and $\omega t = \pi$. This is caused by the maximum influence of the aberration and the Doppler effects at these points, as follows from equation (3).

If we write the logarithm of the relation of neutron intensities in these points we obtain the following result

$$r = \ln \frac{J(\delta, \omega t = 0)}{J(\delta, \omega t = \pi)} = -\frac{2\delta_0 \,.\, \delta_{0t}}{\sigma^2}\,. \tag{13}$$

The dependence $r = r(\delta_0)$ is shown in Fig. 4. Relation (13) predicts the linear relation between the values of δ_0 characterizing the given positions and the corresponding values of r. The experimental results, as can be seen from Fig. 4, show some nonlinearity, which can be explained by the fact, that the rocking curve (Fig. 2) does not precisely fulfil the form of a Gaussian distribution, described by the relation (5).

From expression (13) it is possible to calculate the values of δ_{0t}. If we consider the asymmetry of the rocking curve of the single crystal ($w/2 = 7'$ for $\delta_0 > 0$ and $w/2 = 5'$ for $\delta_0 < 0$) we obtain the value $\delta_{0t} = 0{\cdot}90 \pm 0{\cdot}09$ min of arc. For the obtained values of δ_{0t} we can use equation (4) to calculate the velocity v_p of the motion of crystallographic lattice planes. In this case $v_p = 63 \pm 6$ cm.sec^{-1} for the position $y = 3l/8$ from the quartz bar centre. At the ends of the quartz bar $y = \pm l/2$ and we obtain, for $\bar{v}_0 = u_0\omega$, the value of $\bar{v}_0 = 68 \pm 7$ cm.sec^{-1}.

From equation (2) we can determine the amplitude u_0 of vibrations of the specimen under investigation. For the measured bar we obtained the value $\bar{u}_0 = (4{\cdot}8 \pm 0{\cdot}5) \times 10^{-4}$ cm to which corresponds the relative change in the bar length

$$\Delta\bar{l}/l = (0{\cdot}80 \pm 0{\cdot}08) \times 10^{-4}\,.$$

It follows from our experimental data that the measurements of the time modulation of a neutron beam gives a real possibility of determining the dynamical effects together with a very small velocity of motion of crystallographic lattice planes of the specimen under investigation. This method can be also applied for the measurements of amplitudes of vibrations of single crystals, excited piezoelectrically or by magnetostriction. The velocities of motion of crystallographic lattice planes are of the order of several tens of $cm.sec^{-1}$, and the corresponding amplitudes in the range of 10^{-4} cm.

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X-ray Diffuse Scattering from $NaNbO_3$ as a Function of Temperature

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A qualitative description of the X-ray diffuse scattering from $NaNbO_3$ single crystals as a function of temperature up to 800°C is given. Two types of distinct diffuse scattering where observed in {100} reciprocal planes and on ⟨100⟩ reciprocal axes. While the diffuse scattering in reciprocal planes shows no critical behaviour at the different phase transitions and can be attributed to a 'linear disorder' similar to that suggested earlier for $KNbO_3$, the diffuse scattering on reciprocal axes is critical in the vicinity of the 641°C phase transition. The atomic displacements involved with the linear disorder that persists up to 800°C are attributed to the niobium atoms; the critical planar disorder in the cubic phase is attributed to rotations of oxygen octahedra similar to those suggested for $SrTiO_3$ and $KMnF_3$. Both types of disorder exist in the cubic paraelectric phase.

Introduction

Many recent papers describe experiments in X-ray or neutron scattering from perovskite related compounds [$SrTiO_3$ (Shirane & Yamada, 1969), $KMnF_3$ (Minkiewicz & Shirane, 1969; Minkiewicz, Fujii & Yamada, 1970), $LaAlO_3$ (Plakhty & Cochran, 1968; Axe & Shirane, 1969), $KTaO_3$ (Shirane, Nathans & Minkiewicz, 1967), $PbTiO_3$ (Shirane, Axe, Harada & Remeika, 1970), $BaTiO_3$ (Harada & Honjo, 1967; Comès, Lambert & Guinier, 1968), $KNbO_3$ (Comès, Lambert & Guinier, 1970*a*)]. Nevertheless, the distribution in the reciprocal space of the scattered intensity which provides direct information on atomic displacements that are responsible for the scattering is only known with some precision in the cases of $KNbO_3$ (Comès, Lambert & Guinier, 1970*a*) and $BaTiO_3$ (Shirane, Axe & Harada, 1970; Comès *et al.* 1970*a*). These two crystals, which are isomorphous in all their phases, have structures that always result from a slight distortion of the ideal perovskite unit cell; but they never show multiple-cell structures as can be found for example in $SrTiO_3$ (Müller, 1958; Alefeld, 1969), WO_3 (Ueda & Kobayashi, 1963; Andersson, 1963), $NaNbO_3$ (Vousden, 1951; Bouillaud, 1968), or $KMnF_3$ (Minkiewicz *et al.* 1970; Beckman & Knox, 1961). Thus, it seemed of interest to study the distribution of the diffuse X-ray scattering as a function of temperature in such a mul-

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