

that the ordinary RKKY interaction is stronger than the bound-state interaction at all distances.

To summarize, we have derived an expression for the interaction between two magnetic impurities on the basis of the Nagaoka approach to the problem, and we have reduced the result to an expression that can be evaluated when the one-impurity t matrix is known. (This interaction is not reducible to a simple factor times the spin polarization about one impurity.) To estimate the effect, we have used two forms for the t matrix: Nagaoka's, and Bloomfield and Hamman's. In the former, we can obtain a result analogous to

Nagaoka's long-range polarization if we make manipulations just as he did. But in the latter case, we get an effect an order or two smaller. The results can be adapted to any t -matrix solution,¹¹ but these seemed the most appropriate to use at this time.

¹¹ Recently after the completion of the present paper, E. Müller-Hartmann [Z. Physik **223**, 277 (1969)] published a calculation that indicates a nonoscillatory $(k_F R)^{-3}$ behavior in the spin correlation function at low temperatures. We have searched in this paper for a $(k_F R)^{-2}$ type of effect in the impurity-impurity correlation, but have not yet made an investigation of the details of the nonoscillatory $(k_F R)^{-3}$ terms that Müller-Hartmann suggests may be present.

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Study of the α - β Quartz Phase Transformation by Inelastic Neutron Scattering*

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An inelastic neutron scattering investigation of high-temperature β quartz by triple-axis spectrometry reveals the existence of a phonon branch with anomalously low and temperature-dependent frequencies. Near the Brillouin zone center, the mode is overdamped and unstable, and gives rise to a critical scattering intensity which diverges as $(T - T_c)^{-1}$. Here T_c is 10°C lower than the transition temperature $T_0 = 573^\circ\text{C}$. Measurements of the relative intensity of the critical scattering about various reciprocal-lattice points establishes that the general pattern of displacements associated with the α - β transformation is determined by this soft mode. At room temperature, the zone center phonon at 25.8 meV (208 cm^{-1}) is shown to strongly resemble the α - β displacements. This confirms the proposal by Scott that the renormalized soft mode interacts with and passes through another low-lying excitation. It is suggested that the anomalous elastic behavior of β quartz results from virtual excitation of pairs of phonons in the soft branch with wave vectors directed oppositely along the hexagonal axis.

I. INTRODUCTION

AT about 573°C , quartz undergoes a transformation from a high-temperature hexagonal β form (space group D_6^4 or its enantiomorph D_6^5) into a trigonal α form (D_3^4 or D_3^6) which differs from the former by loss of 180° rotational symmetry about the c axis. The atomic displacements involved are shown in Fig. 1. It has long been suspected that phonons were actively involved in the mechanism of the α - β transformation.¹⁻³ By analogy with the mechanism for several ferroelectric phase changes, one is tempted to suppose that the

transformation results from an instability of a normal vibrational mode of the crystal.⁴ The several problems encountered in applying these ideas to quartz have been reviewed by Scott,⁵ and basically arise from the following points:

(1) Although recent light scattering experiments by Shapiro, O'Shea, and Cummins⁶ have established the existence of an excitation whose frequency does decrease remarkably as the transformation temperature T_0 is approached from below, its presence has raised fundamental questions concerning the normal-mode assignments in quartz and leaves the nature of the unstable excitation unclear.

* Work performed under the auspices of the U. S. Atomic Energy Commission.

¹ C. V. Raman and T. M. K. Nedungadi, *Nature* **144**, 147 (1940).

² P. K. Narayanaswamy, *Proc. Indian Acad. Sci.* **A28**, 417 (1948).

³ D. A. Kleinman and W. G. Spitzer, *Phys. Rev.* **125**, 16 (1962).

⁴ W. Cochran, *Advan. Phys.* **10**, 401 (1961).

⁵ J. F. Scott, *Phys. Rev. Letters* **21**, 907 (1968).

⁶ S. M. Shapiro, D. C. O'Shea, and H. Z. Cummins, *Phys. Rev. Letters* **19**, 361 (1967).

(2) The dramatic increase in the intensity of scattered light as T_0 is approached from below,⁷ which has been interpreted as arising from divergent dynamical fluctuations in the structure,⁸ has recently been reported to be quite static in character and presumably due to extensive microtwinning which is known to accompany the transformation.⁹ Low-angle x-ray scattering, involving scattering vectors comparable to those of the light scattering experiments, have also failed to detect critical scattering.¹⁰

(3) There is no published evidence, optical or otherwise, of unstable excitations or critical phenomena in the high-temperature β phase,¹¹ although such evidence would obviously be of great value in any detailed understanding of the transition mechanism. Elcombe¹² has carried out the most extensive inelastic neutron scattering investigation to date, but she did not detect a soft Brillouin zone (BZ) center optic phonon. Symmetry considerations show such a mode to be both infrared and Raman inactive.

We wish to report some results of inelastic neutron scattering experiments which establish the existence of critical fluctuations in the β phase. These fluctuations approximately follow a simple Curie law and appear to result from an optical phonon branch which is overdamped near the BZ center. We are also able to make some rather detailed estimates of the atomic displacements associated with critical fluctuations of the β phase on one hand, those of the unstable excitation of the α phase on the other, and their relation to the (static) spontaneous displacements associated with the α - β transformation itself. A close similarity between these quantities is required in a second-order transformation¹³ and is to be approximately expected for first-order transformations as well, provided the discontinuity is not too great.

II. CRITICAL SCATTERING IN β QUARTZ

Two samples of Brazilian quartz ($2 \times 2 \times 2$ and $3 \times 3 \times 3$ cm), supplied by Valpey Corp., were studied. The temperature was regulated within $\pm 1^\circ\text{C}$ for any

⁷ I. A. Yakovlev, T. S. Velichkina, and L. F. Mikheeva, Dokl. Akad. Nauk SSSR **5**, 675 (1956) [English transl.: Soviet Phys.—Doklady **1**, 215 (1956)]; I. A. Yakovlev and T. S. Velichkina, Soviet Phys.—Usp. **63**, 552 (1957).

⁸ V. L. Ginsburg and A. P. Levanyuk, J. Phys. Chem. Solids **6**, 51 (1958); Zh. Eksperim. i Teor. Fiz. **39**, 192 (1960) [English transl.: Soviet Phys.—JETP **12**, 138 (1961)]; V. L. Ginsburg, Usp. Fiz. Nauk **77**, 621 (1962) [English transl.: Soviet Phys.—Usp. **5**, 649 (1963)].

⁹ S. M. Shapiro and H. Z. Cummins, Phys. Rev. Letters **21**, 1578 (1968); S. M. Shapiro, Ph.D. thesis, Johns Hopkins University, 1969 (unpublished).

¹⁰ H. Brumberger, W. Claffey, N. G. Alexandropoulos, and D. Hakim, Phys. Rev. Letters **22**, 537 (1969).

¹¹ We have learned by private communication through J. Harada that strongly temperature-dependent diffuse x-ray scattering about T_0 has been observed by K. Ishida and G. Honjo (unpublished).

¹² M. M. Elcombe, Ph.D. thesis, Cambridge University, 1966 (unpublished); Proc. Phys. Soc. (London) **91**, 947 (1967).

¹³ P. C. Kwok and P. B. Miller, Phys. Rev. **151**, 387 (1966).

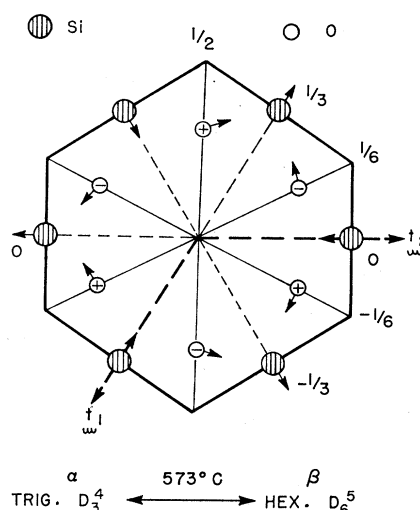


Fig. 1. A projection on the basal plane of the Wigner-Seitz unit cell of β quartz. The arrows indicate the shifts in atomic positions between the β phase and the room-temperature α phase.

given experiment. All of the high-temperature measurements were made with the scattering vector in the ($h0l$) zone of the reciprocal lattice. Some additional room-temperature measurements were performed in the ($hk0$) zone. All measurements were carried out on a triple-axis spectrometer at the Brookhaven High Flux Beam Reactor in the "constant Q " mode with fixed incident neutron energies ranging between 19 and 78 meV.

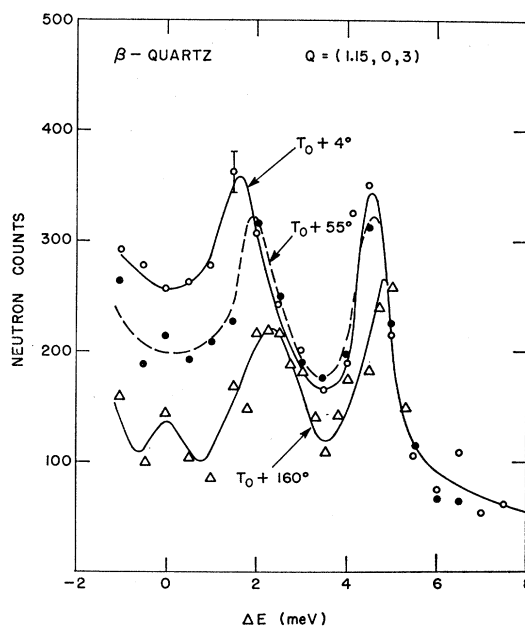


Fig. 2. Temperature dependence of scattering from low-energy excitations in β quartz. The scattering vector Q is specified by components of the hexagonal reciprocal lattice.

The principal difficulties involved in detecting low-frequency BZ center optic modes are caused by the simultaneous presence of strong elastic Bragg scattering and more importantly, scattering from nearby acoustic branches. Preliminary calculations suggested several reciprocal-lattice points with relatively weak Bragg and acoustic phonon cross sections for which scattering from fluctuations proportional to the displacements shown in Fig. 1 should be strong. Figure 2 shows an example of the neutron groups observed about one such reciprocal-lattice point, (1,0,3) at several temperatures just above T_0 . Similar data taken at various points in reciprocal space along the [100] axis have been used to construct the set of partial dispersion curves shown in Fig. 3. Unlike the upper branch, whose slope at finite q agrees closely with the velocity of transverse sound, the lower branch is clearly not acoustic in the normal sense. It does not extrapolate to $\omega \rightarrow 0$ as $q \rightarrow 0$, nor does its slope match any acoustic velocity, and it displays a

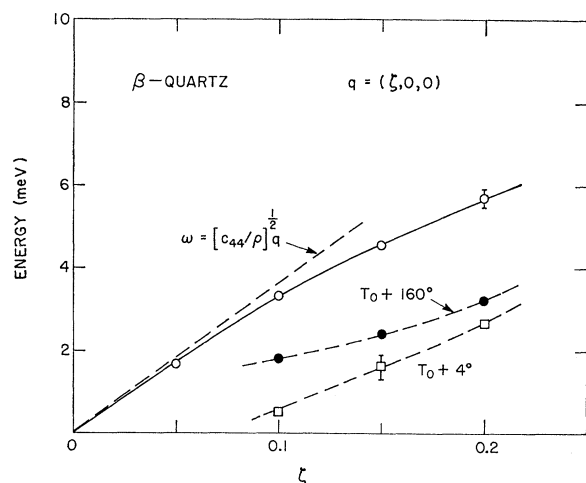


FIG. 3. Partial phonon dispersion curve in β quartz for $q = (\zeta, 0, 0)$. The upper branch is a transverse acoustic mode. The lower branch, which displays a strong temperature dependence, is associated with the soft optic branch. The energies are peaks of neutron groups and may differ significantly from the quasi-harmonic frequencies due to damping effects.

remarkably strong temperature dependence. This branch is either the soft optic branch itself, or is the remaining transverse acoustic branch which has been severely deformed through interaction with the soft optic branch. Because the reduced symmetry at $(\zeta, 0, 0)$ permits such interaction, the distinction between acoustic and optic branches is somewhat academic in any event.

Since the size of the unit cell does not change as a result of the transformation, any phonon instability must first occur at the BZ center. Figure 4 shows an energy analysis of the scattering at the BZ center ($Q=1, 0, 3$) at several temperatures above T_0 . The strong central Bragg peak is seen to be superimposed upon a weaker peak which grows in strength and

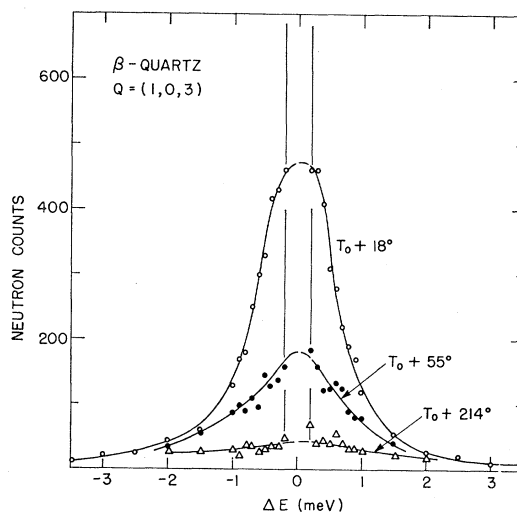


FIG. 4. Energy analysis of scattering about the (1,0,3) reflection in β quartz at several temperatures above T_0 . The strong central Bragg peak is superimposed upon weaker critical inelastic scattering.

narrows in half-width as T_0 is approached from above. With varying degrees of visibility, similar behavior can be observed about several other Bragg reflections. By interpolation of the profile of this weaker peak through the region of strong Bragg scattering, it is possible to estimate the integrated intensity of the temperature-dependent component of the scattering, as shown in Fig. 5. Data taken at two different incident

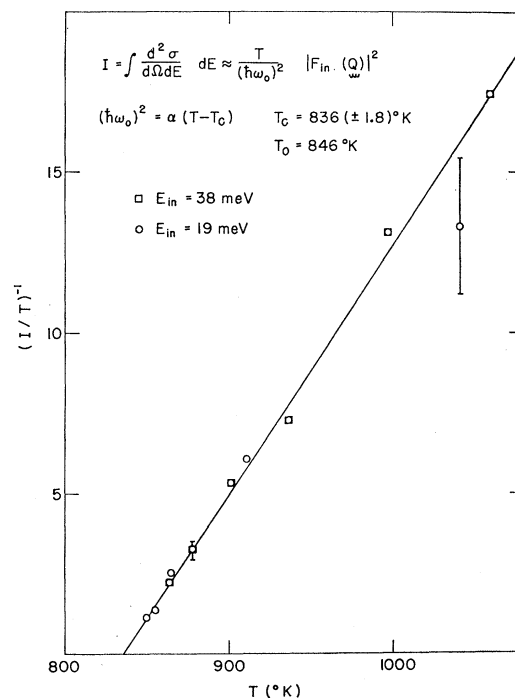


FIG. 5. Temperature dependence of the integrated scattering intensity for the (1,0,3) reflection, plotted in such a way as to demonstrate the Curie law divergence.

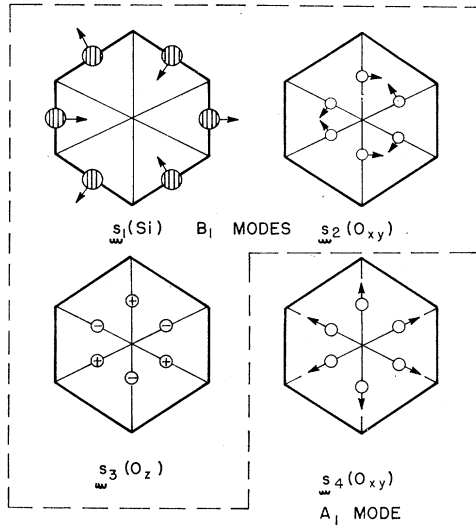


FIG. 6. Symmetry mode vectors used to describe the displacements associated with the α - β quartz transformation.

energies are in good agreement and minimize the probability of errors due to finite resolution.

The divergent behavior of the scattering intensity establishes it as true critical scattering, which can be most easily understood as arising from an overdamped vibrational excitation associated with the soft branch shown in Fig. 3. The one-phonon scattering cross section $d^2\sigma/d\Omega dE$ for thermal neutrons with a single normal vibrational mode is proportional to¹⁴

$$\left(\frac{d^2\sigma}{d\Omega dE}\right) \propto \left|\frac{k'}{k}\right| |F_{\text{in}}(\mathbf{Q})|^2 [1+n(\omega)] A(\omega), \quad (1)$$

where $\hbar(\mathbf{k}'-\mathbf{k})=\hbar\mathbf{Q}$ and $(\hbar^2/2m)(k'^2-k^2)=\hbar\omega$ are, respectively, the momentum and energy transfer. $F_{\text{in}}(\mathbf{Q})$ is the inelastic structure factor for the normal mode and $n(\omega)$ is the phonon occupation number. For present purposes, the spectral correlation function $A(\omega)$ can be assumed to have the form¹⁵

$$A(\omega) = \frac{1}{\pi} \frac{2\omega\Gamma}{(\omega_0^2 - \omega^2)^2 + (\omega\Gamma)^2}. \quad (2)$$

With weak damping ($\Gamma \ll \omega_0$), $A(\omega)$ is strongly peaked about the harmonic frequencies $\pm\omega_0$. But in the overdamped condition ($\Gamma^2 > 2\omega_0^2$, favored by high temperatures and low harmonic frequencies), the spectral profile is a single peak centered about $\omega_0=0$, in qualitative agreement with our observations. Although in such cases ω_0 is not directly obtainable from the spectral profile, information concerning the temperature dependence of ω_0 can be conveniently obtained from the

integrated intensity. Using the high-temperature approximation, $n(\omega) \approx 1+n(\omega) = kT/\hbar\omega$, Eq. (1) may be integrated to give

$$I = \int \frac{d^2\sigma}{d\Omega dE} dE \propto |F_{\text{in}}(\mathbf{Q})|^2 \frac{T}{\omega_0^2}, \quad (3)$$

showing the integrated intensity to be independent of damping. The data of Fig. 5 have been plotted in such a way as to exhibit the temperature dependence of ω_0^2 , assuming Eq. (3) to be applicable. It appears that the simple linear relation $\omega_0^2 = \alpha(T - T_c)$, which approximately characterizes unstable phonon modes in most displacive transformations, is adequate to represent the observations. The discrepancy between T_0 and T_c supports the conclusion of other recent investigations that the transformation is of first order,^{9,16} but the relatively small magnitude of the difference, together with the observed critical scattering, make it clear that it is nearly of second order. No comparable critical scattering was observed below T_0 .

Evidence for mode overdamping has been seen recently in other systems undergoing displacive transformations, and in most of these systems it has proven possible to undamp the condensing mode at sufficiently high temperatures.¹⁷ In β quartz the critical scattering at the BZ center, although it becomes quite weak, appears to remain centered about $\Delta E=0$. (An upper temperature limit is imposed by the quartz-tridymite transformation at $\approx 850^\circ\text{C}$.) It should also be mentioned

TABLE I. Symmetry mode vectors and displacements in the α - β quartz transformation (expressed in hexagonal coordinates with $x=0.2068$).

| Atom | Position in β phase | General displacement |
|---|--|--------------------------------|
| Si(1) | $(0, \frac{1}{2}, 0)$ | $(0, S_1, 0)$ |
| Si(2) | $(\frac{1}{2}, 0, \frac{1}{2})$ | $(S_1, 0, 0)$ |
| Si(3) | $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ | $(-S_1, -S_1, 0)$ |
| O(1) | $(-x, x, \frac{1}{6})$ | $(S_2+S_4, S_2-S_4, -S_3)$ |
| O(2) | $(-2x, -x, \frac{1}{2})$ | $(2S_4, -S_2+S_4, S_3)$ |
| O(3) | $(-x, -2x, -\frac{1}{6})$ | $(-S_2+S_4, 2S_4, -S_3)$ |
| O(4) | $(x, -x, \frac{1}{6})$ | (S_2-S_4, S_2+S_4, S_3) |
| O(5) | $(2x, x, -\frac{1}{2})$ | $(-2S_4, -S_2-S_4, -S_3)$ |
| O(6) | $(x, 2x, -\frac{1}{6})$ | $(-S_2-S_4, -2S_4, S_3)$ |
| Symmetry coordinates of 207-cm ⁻¹ mode | | |
| | Present study | Model calculation ^a |
| S_1/S_2 | 0.54(± 0.17) | 0.80 |
| S_3/S_2 | -0.80(± 0.05) | -0.60 |
| S_4/S_2 | 0.28(± 0.06) | 0.20 |
| Spontaneous displacements associated with $\beta \rightarrow \alpha$ ^b | | |
| | | |
| | | 0.490(± 0.019) |
| | | -0.802(± 0.037) |
| | | 0.013(± 0.052) |

^a See Ref. 3.

^b See Ref. 15.

¹⁴ P. C. Kwok, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1967), Vol. 20, p. 233.

¹⁵ See, for example, M. Lax, *J. Phys. Chem. Solids* **25**, 487 (1964).

¹⁶ R. A. Young, U. S. Air Force Report No. AFOSR-2569, and Defense Documentation Center Report No. AD 276235, 1962 (unpublished).

¹⁷ V. J. Minkiewicz and G. Shirane, *J. Phys. Soc. Japan* **26**, 674 (1969); J. D. Axe and G. Shirane, *Phys. Rev.* **183**, 820 (1969).

that with q along $[001]$, the only other direction in reciprocal space that was investigated, there was no clear evidence of an undamped soft branch. In fact, it appears likely that the soft branch remains overdamped well out into the BZ in this direction.

III. DESCRIPTION OF CRITICAL MODES

Information about the atomic displacements giving rise to the critical scattering observed at the BZ center was obtained from a study of the relative intensity of the scattering about different reciprocal-lattice points. The inelastic structure factor of Eq. (1) can, for BZ center phonons, be written

$$F_{\text{in}}(\mathbf{Q}) = \sum_k (\mathbf{Q} \cdot \boldsymbol{\xi}_k) b_k e^{-W_k} e^{i\mathbf{Q} \cdot \mathbf{R}_k}, \quad (4)$$

where b_k is the neutron scattering length, e^{-W_k} is the Debye-Waller factor of the nucleus at position \mathbf{R}_k within the unit cell, and $\boldsymbol{\xi}_k$ is the normalized displacement amplitude of this nucleus in the normal mode. Elementary symmetry considerations dictate that the unstable symmetry breaking mode must transform according to the B_1 irreducible representation of the point group D_6 , the $q=0$ factor group for β quartz. Accordingly, it is convenient to represent the most general B_1 displacement as

$$\boldsymbol{\xi}_k(B_1) = \sum_{\lambda=1}^3 S_{\lambda} \mathbf{s}_k(B_1, \lambda), \quad (5)$$

where the symmetry mode vectors $\mathbf{s}_k(B_1, \lambda)$ have definite transformation properties but are otherwise arbitrarily defined in Table I and depicted in Fig. 6.

We have attempted to obtain a set of parameters S_{λ} which describe the critical scattering above T_0 by a least-squares fitting of $|F_{\text{ino}}(\mathbf{Q})|^2$ [Eq. (4)], to intensity data similar to that of Fig. 4, but taken about 13 different $(h0l)$ lattice points. Atomic positions and anisotropic Debye-Waller factors determined by x-ray analysis were used.¹⁶ The problem of background subtraction was severe, and the results were only modestly successful as can be seen in Fig. 7. The results are, however, sufficiently precise to demonstrate how the general features of the $\beta \rightarrow \alpha$ transformation are determined by the critical fluctuations.

We have also made some room-temperature measurements which have bearing on the current puzzle concerning the BZ center normal-mode assignments in α quartz. The interpretation of the Raman scattering spectra is complicated by the appearance of an extra totally symmetric (A_1) mode, and it has been by no means clear what the nature of the extra mode is, nor in fact which of the five features with A_1 symmetry properties is to be considered the extra one. Since one of the five is the one whose frequency tends to zero near T_0 , the problem is one which cannot be ignored in any discussion of the mechanics of the α - β transformation. Scott⁵ has proposed that the extra mode is a

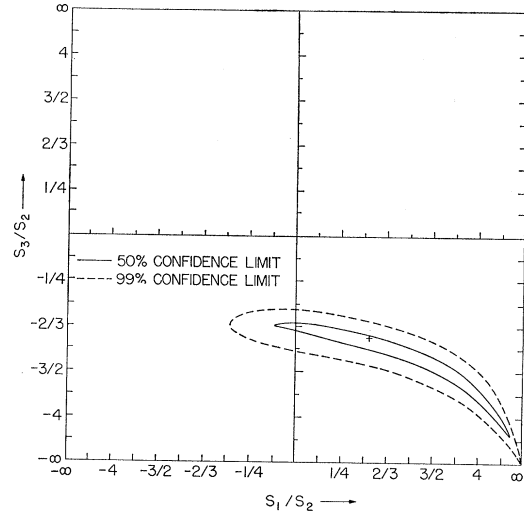


FIG. 7. Determination of the relative atomic displacements associated with the critical neutron scattering. Statistically, there is a 50% probability of the true ratios lying within the inner contour, a 99% probability of lying with the outer contour. The spontaneous $\beta \rightarrow \alpha$ displacements are indicated by the cross.

two-phonon excitation which at room temperature lies below the soft one-phonon mode (147 and 208 cm^{-1} , respectively) but that as the temperature is raised, the frequency of the soft mode decreases, and the two types of excitations become thoroughly mixed because of anharmonic coupling. Near T_0 , the excitations are once again distinct, the one-phonon mode now being the lowest-frequency component. If this explanation is correct, the room temperature renormalized soft mode is not at 147 cm^{-1} as initially proposed⁶ but is rather at 208 cm^{-1} . To test this assumption, we repeated the mode determination procedure described above for the 208- cm^{-1} excitation with more unambiguous results as shown in Fig. 8. Because of the reduced symmetry of the low-temperature phase, an additional displacement $S_4 \mathbf{s}_k(A_1)$ must be included with those of Eq. (5) in order to completely describe a totally symmetric mode.¹⁸ The results, shown in Table I demonstrate a remarkable similarity between this mode and the displacements involved in the α - β transformation. There can thus be little doubt that this is the renormalized soft mode, and that it passes through the lower 147- cm^{-1} excitation as the temperature is raised. Also included for comparison in Table I, is the eigenvector for the 208- cm^{-1} mode deduced from a lattice dynamical calculation by Kleinman and Spitzer.³ The calculated values show a reversal of the relative importance of the

¹⁸ The correlation of the symmetry properties of the BZ center phonons between the $q=0$ factor groups of the two phases ($D_6 \rightarrow D_3$) is $A_1 + 3B_1 \rightarrow 4A_1'$, so that A_1 and B_1 modes become mixed in the α phase. The amount of mixing, which depends upon the proximity of the uncoupled modes, is not expected to be large for the renormalized soft mode. Our results indicate a rather larger amount of A_1 character than was anticipated, and may be connected with the still finite coupling with the 147- cm^{-1} excitation.

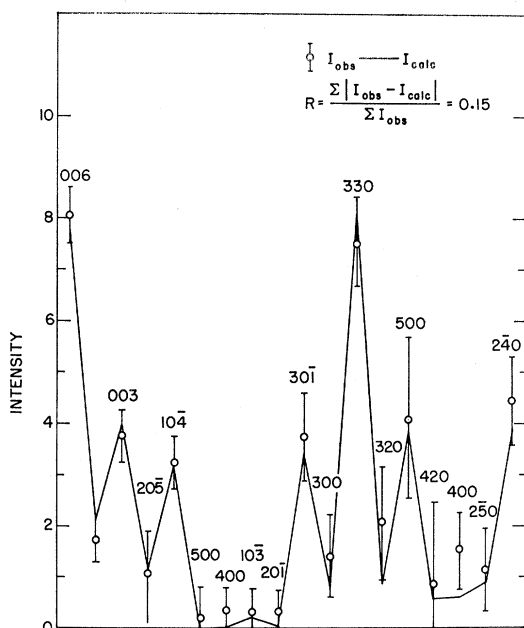


FIG. 8. A comparison of calculated and observed inelastic scattering intensities for the 208-cm⁻¹ mode in α quartz at various reciprocal-lattice points.

S_1 and S_3 contributions, but the qualitative agreement is quite evident. Elcombe¹² has also performed some lattice dynamical calculations for both the α - and β -phase, and reports that the calculated B_1 mode frequency is low in the β phase and increases rapidly as the structure changes from β to α .

An attempt to study the temperature dependence of this 208-cm⁻¹ mode was frustrated by the rather remarkable broadening which accompanied the increasing temperature, as shown in Fig. 9. It is likely that the mode interaction proposed by Scott is largely responsible for this effect. Other modes (e.g., the 128-cm⁻¹ E mode) could be observed at the same temperature with no difficulty. At room temperature, there is only the barest suggestion of scattering from the 147-cm⁻¹ (18.2 meV) A_1 excitation. For any given fixed scattering vector \mathbf{Q} , the scattering cross section for two-phonon excitation is smaller than the one-phonon excitation by approximately the factor $(m/M) \times [2n(\bar{\omega}) + 1]$, m being the neutron mass, M is the average mass of the constituent atoms, and $n(\bar{\omega})$ is an average phonon occupation number. Since this cross section is further distributed over the energy range spanned by the two-phonon density of states, we would expect to observe this process only with great difficulty in these experiments. Multiple-phonon Raman scattering is governed by entirely different considerations (nonlinear electron-lattice coupling) and can in some cases dominate one-phonon scattering.¹⁹

¹⁹ J. R. Hardy, in *Phonons: Scottish Universities' Summer School 1965*, edited by R. W. H. Stevenson (Oliver and Boyd, Edinburgh, 1966), p. 245.

IV. ELASTIC BEHAVIOR OF β QUARTZ

Of the various changes in physical properties associated with the α - β transformation, perhaps the most striking occur in the elastic constants, as shown in Fig. 10 for β quartz.²⁰ Miller and Axe²¹ called attention to the fact that if the elastic constants were separated into temperature-dependent and temperature-independent terms, $c_{ij} = c_{ij}^0 + c_{ij}'(T)$, the temperature-dependent terms, were interrelated in a way not required by over-all symmetry conditions, namely,

$$c_{11}' = c_{12}', \quad c_{11}'c_{33}' = (c_{13}')^2, \quad \text{and} \quad c_{44}' = 0. \quad (6)$$

These authors went on to show how this behavior could be accounted for by a large internal strain contribution to the elastic constants due to a soft temperature-dependent $q=0$ optic phonon mode, but only if the soft mode possessed totally symmetric (A_1) transformation properties in the β phase. Since the condensation of a symmetric mode does not lead to a change in symmetry, one must further postulate another independent soft B_1 optic mode in order to explain the transformation itself. This is a rather unappealing concept, but as we have noted, at the time there was sufficient uncertainty concerning the normal-mode assignments⁶ to warrant consideration of this proposal.

Now, however, it seems rather clear that there is but a single soft-phonon branch of B_1 rather than A_1 symmetry at $q=0$ which must, in any satisfactory understanding of the α - β transformation, account for the elastic behavior shown in Fig. 10. It appears that this is possible by extending the analysis mentioned above.²¹

The internal strain contribution to the elastic response can be thought of as a virtual excitation of an harmonically coupled $q=0$ optical phonon. There is a

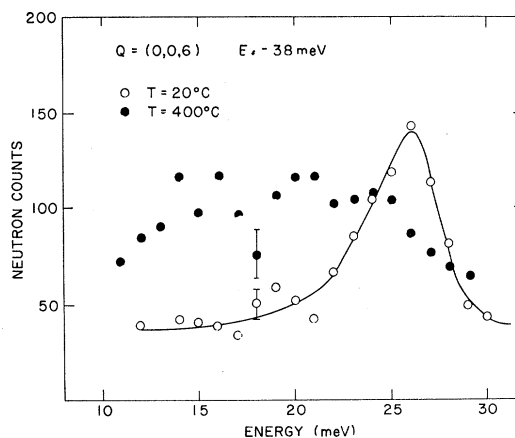


FIG. 9. Inelastic neutron scattering about the (006) reflection in α quartz, illustrating the extreme broadening of the 208-cm⁻¹ (25.8 meV) $q=0$ phonon mode with increasing temperature.

²⁰ E. W. Kammer, T. E. Pardue, and H. F. Frissel, *J. Appl. Phys.* **19**, 265 (1948).

²¹ P. B. Miller and J. D. Axe, *Phys. Rev.* **163**, 924 (1967).

closely related higher-order anharmonic contribution which consists of a virtual excitation of optical phonon pairs at $(j\mathbf{q})$ and $(j-\mathbf{q})$, (j is a branch index). In the high-temperature limit $[kT \gg \hbar\omega(j\mathbf{q})]$, this contribution is given by^{22,23}

$$c'_{\alpha\beta\gamma\lambda}(jj\mathbf{q}) = -(8\pi^3/Nv_a)F_{\alpha\beta}(jj\mathbf{q})F_{\gamma\lambda}(jj-\mathbf{q}) \times kT/\omega^4(j\mathbf{q}), \quad (7)$$

where

$$F_{\alpha\beta}(jj\mathbf{q}) = \sum_{l'k\lambda k'\gamma} [\sum_{\bar{l}} i_{\bar{l}} \Phi_{\alpha\lambda\gamma}(\bar{l}k; 0k; l'k') R_{\beta}(\bar{l}k)] \times \xi_{\lambda k}(j\mathbf{q}) \xi_{\gamma k'}(j-\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{R}(l')}. \quad (8)$$

Here $\Phi_{\alpha\lambda\gamma}$ is the conventional third-order anharmonic potential constant, $\mathbf{R}(\bar{l}k)$ is the equilibrium position vector of the k' th atom in the l' th cell, with mass m_k . As previously $m_k^{1/2}\xi_k(j\mathbf{q})$ are the normalized harmonic polarization vectors and N is the total number of cells each with volume v_a . Typically, each mode pair contributes a fraction of order $N^{-1}(u/d)^2$ to the elastic response, u being an rms atomic thermal amplitude, and d is the nearest internuclear distance, so that the net effect is small. It is clear, however, from the form of Eq. (7) that a large number of modes occurring in a soft branch could lead to a substantial effect.

By considering the symmetrized contributions to the elastic constant $\sum_R c'_{\alpha\beta\gamma\lambda}(jjR\mathbf{q})$, where $R\mathbf{q}$ comprise the star of \mathbf{q} , it is possible to show that the symmetry relations given in Eq. (6) are a unique result of the following relations among the components of the $\mathbf{F}(jj\mathbf{q})$ tensor:

$$F_{xx} = F_{yy}; \quad F_{zz} \neq 0; \quad \text{all other } F_{ij} = 0. \quad (9)$$

The symmetry properties of the $\mathbf{F}(jj\mathbf{q})$ tensor depend upon the direction of \mathbf{q} and can be discussed in terms of the operations of the rotation group of the wave vector \mathbf{q} .²⁴ In what follows, we consider only the soft-phonon branch, i.e., phonons with finite \mathbf{q} with symmetry compatible with B_1 at $\mathbf{q}=0$. There are no symmetry requirements upon $\mathbf{F}(jj\mathbf{q})$ for general \mathbf{q} , and the requirements imposed when \mathbf{q} is in the a - b plane are not those of Eq. (9). Such relations do obtain when \mathbf{q} is directed along the c axis, however, as the following argument reveals. Since the quantity in brackets in Eq. (8) is a characteristic tensor of the undistorted crystal, $\mathbf{F}(jj\mathbf{q})$ must transform as the product

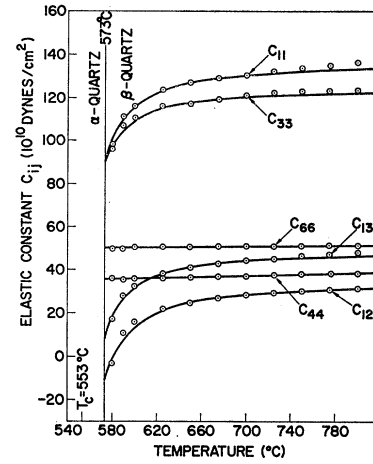


FIG. 10. The temperature dependence of the elastic constants of β quartz. Open circles are measured values (Ref. 19). The solid lines are given by $c_{ij} = c_{ij}^0 - \Delta c_{ij}/(T - T_c')$, with $\Delta c_{11} = \Delta c_{12}$; $(\Delta c_{11}, \Delta c_{33}) = (\Delta c_{13})^2$; $\Delta c_{44} = c_{66} = 0$; and $T_c' = 553^\circ\text{C}$ (Ref. 20).

$[\xi(j\mathbf{q})\xi(j-\mathbf{q})]$, in this case the A_1 representation, of the point group D_6 . But $\mathbf{F}(jj\mathbf{q})$ must also transform as a second-rank tensor and a totally symmetric second-rank tensor of D_6 is just of the form given in Eq. (9).

The only likely explanation which could be given for the dominance of modes with \mathbf{q} along c is that the $\omega(j\mathbf{q})$ are especially low along or nearly along this direction. This nicely complements our tentative conclusion that the soft branch remains overdamped (and thus probably at low frequency) in this direction for very considerable values of $|q|$ at temperatures well above T_0 . Making the simple but reasonable assumption that $\omega^2(j\mathbf{q}) = \omega^2(j0) + \alpha(q_x^2 + q_y^2) + \beta q_z^2$ with $\alpha \gg \beta$, and further neglecting the \mathbf{q} dependence of $\mathbf{F}(jj\mathbf{q})$ for \mathbf{q} nearly along c , leads to a total contribution to the elastic constants of the form

$$\int d\mathbf{q} c_{\alpha\beta\gamma\lambda'}(jj\mathbf{q}) \approx 1/\omega^2(j0) \approx (T - T_c)^{-1} \quad (10)$$

for temperatures such that the frequency dispersion of the soft-mode branch in the c direction is small compared to $\omega(j0)$. The observed data are approximately fit by such a relation.²¹ (See Fig. 10.)

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²² M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954).

²³ R. A. Cowley, *Advan. Phys.* **12**, 421 (1963).

²⁴ M. Lax, *Phys. Rev.* **138**, A793 (1965); A. A. Maradudin and S. H. Vosko, *Rev. Mod. Phys.* **40**, 1 (1968). In the present case, no further symmetry requirements are introduced by time reversal symmetry.