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Measurement of the order parameter of α-quartz by second-harmonic generation of light*

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We discuss the concept of an order parameter η for the α-β transition of quartz following Landau's theory. Some physical properties, among them the second-harmonic-generation coefficient are found to vary as η, while others vary as η^2. A measurement of d_{11} from room temperature to the transition is described. Assuming that $d_{11} = \eta$ one obtains the temperature variation of the order parameter; our data are in good agreement with Landau's theory. They also agree with the temperature variation of other properties, particularly birefringence, thermal dilatation, and some elastic constants. Our data can also be fitted to a formula $\eta = \eta^* + C(t - t^*)^\beta$, with a critical exponent $\beta = 1/3$ from room temperature to the transition, or with $\beta = 1/6$ and $\eta^* = 0$ from 520 to 573.2 °C the transition temperature. We show that this is not fortuitous but that one can always find these exponents in making a four- or three-parameter fit to Landau's formula. Thus, in general, there is considerable ambiguity when one tries to fit critical exponents to a first-order transition.

I. INTRODUCTION

Silicon dioxide, SiO_2, possesses several different equilibrium states as a function of temperature and pressure.[1] The stable phase at room temperature under atmospheric pressure is crystalline quartz, which is called low quartz or α-quartz to distinguish it from another closely related high-temperature phase, called high quartz or β-quartz. Since its discovery by Le Chatelier in 1889,[2] this phase transition, which occurs at 573 °C, has been the subject of many investigations. The earlier ones were reviewed, in considerable details, by Sosman in his book on silica phases (1927).[3] More recent but less extensive data are found in a partial revised edition of Sosman's book (1965).[4] The dynamical aspects of the transition have recently been reviewed by Scott.[5]

A point which for some time had been the subject of most discussions is the existence or not of a discontinuity at the transition. Most of the earlier data (among them the first ones by Le Chatelier) show a discontinuity. Keith and Tuttle in an extensive study of small variations of the transition temperature among many samples by differential thermal analysis obtained a temperature hysteresis of about 1 °C between heating and cooling[6]—which is the mark of a first-order transition. But other experiments showed singularities characteristic of a second-order transition, for example, the increase of the specific heat in a measurement by Sinel'nikov,[7] or the intense scattering of light close to the transition temperature observed by Yakolev *et al.*[8,9] Indeed most experiments were not sensitive enough to show clearly a small discontinuity which can be masked by the sharp variation of many properties of quartz in a temperature range of a few tens of degrees below the transition temperature T_t and of a few degrees above T_t. Cohen and Klement used Pippard's relation, valid for a second-order or λ-point transition to correlate the temperature variation of several physical properties near T_t.[10,11] Coe and Paterson, who also made comparisons between several physical properties successively with the hypothesis of first- and second-order transition, favored slightly the first hypothesis.[12] The existence of a discontinuity was observed unambiguously in 1968 by Shapiro and Cummins in a study of light scattering (Raman, Brillouin, and Rayleigh scattering) near the transition.[13,14] The same conclusion was also reached by Höchli[15] in a measurement of the elastic constant C_{14}.

In this paper we present a measurement of a phenomenon which is very sensitive to symmetry change produced by the α-β transition, the second-harmonic generation (SHG) of light.[16] In Sec. II we discuss the concept of an order parameter in quartz and its relation to SHG, and other physical properties. In Sec. III the experiment is described and we deduce the variation of the nonlinear susceptibility from room temperature to the transition temperature. This result is compared in Sec. IV with measurements of other properties of quartz (birefringence, thermal expansion, elastic constants) and is interpreted following Landau's theory of phase transitions. In Sec. V we discuss the relation between the result of Landau's theory with other formulas with critical exponents which have been proposed for first-order transition and we show that in the case of α-quartz, experiments to differentiate them would be difficult.

II. ORDER PARAMETER OF α-QUARTZ AND ITS RELATION TO THE NONLINEAR SUSCEPTIBILITY

Since there are three molecules of SIO_2 in the unit cell of quartz there are 27 degrees of liberty. Atomic displacements, as a function of temperature are known from the x-ray work of Young.[17] Phonon dispersion curves have been measured and a soft mode found by neutron measurements.[18] A simple model with rotation of rigid tetrahedra has been used recently by Grimm and Dorner to describe the transition, but to take into account at the same time atomic displacements and macroscopic expansion they have to also introduce a deformation of the tetrahedra.[19] In this paper we give only a phenomenological discussion of the transition, following symmetry arguments.

In the two phases considered, quartz has the same number of atoms per unit cell. The point group of α-phase is (32). The Z axis is along the rotation axis of order 3, X along one of the axes of order 2. The point group of the β-phase is (622). So in going from the β to the α phase the crystal loses a twofold axis (Y_2) along Y. The free energy F can be written as a function of the polarization P_i ($i=1$ to 3) and of the strain u_j ($j=1$ to 6 with Voigt's convention):

$$F=\alpha_i P_i^2+C_{jl}u_j u_l+a_{ij}P_i u_j \;, \tag{1}$$

where α_i is the inverse susceptibility (tensor of rank 2) C_{jl} the compliance tensor (rank 4), a_{ij} the piezoelectric tensor (rank 3). In α phase, F is invariant under all symmetry operations of (32). If, furthermore, we apply (Y_2) the tensor coefficients in (1) remain invariant except C_{14}, C_{41} and a_{11}, which change their sign. In β-phase these coefficients are zero and cooling from β phase, two equivalent orientations are available for X which may lead to Dauphiné twinning.[1] These transformation properties of C_{14} and a_{11} under the symmetry elements of (622) belong to the B_1 representation.[14] Following Landau[20] we introduce an order parameter η which describes all the changes produced by the transition, and so belongs to the B_1 representation of (622). The lowest rank for a tensor belonging to B_1 is rank 3, so η is similar to the piezoelectric constant a_{11} (this result has been previously obtained by Aizu[21]; a similar analysis is valid for NH_4Cl). a_{11} and C_{14} belong to the same representation as η and can be expressed as an odd function of η. The other coefficients invariant under (Y_2) belong to the totally symmetric representation A_1, as does η^2, and they can be expressed as even functions of η. In a second-order transition according to Cochran[22] there is generally a soft mode which has the same symmetry properties as the order parameter, and which produces the transition. But in a first-order transition complications can occur. As there is a discontinuity, the soft mode does not need to have atomic displacements similar to those produced by the transition. However from the neutron experiment of Axe and Shirane,[18] it seems that the soft mode in β-phase is a B_1 mode closely related to atomic displacements in the α-phase. But the anomalous variation of some elastic constants in the β-phase shows that at least there is strong anharmonic coupling of fluctuations to deformation.[18,23] Attempts have even been made to explain the transition by an acoustic instability.[24,25] To describe the transition, we begin with the full expression of $F(\eta, u, P)$ and then we solve

$$\frac{\partial F}{\partial \eta}=0,\quad \frac{\partial F}{\partial u}=\sigma,\quad \frac{\partial F}{\partial P}=E\;, \tag{2}$$

where σ and E are the external stress and electric field. Taking the last two equations for a free crystal ($\sigma=E=0$) and eliminating u and P we obtain a function of η, with only even powers of η, which can be expanded as

$$F=\tfrac{1}{2}a\eta^2+\tfrac{1}{4}b\eta^4+\tfrac{1}{6}c\eta^6+\cdots\;. \tag{3}$$

This is the usual Landau free energy which has been used previously for quartz by Ginzburg[26] to explain the critical opalescence observed by Yakolev *et al.*[8,9] We assume that $a=t-t_0$. If $b>0$ one has a second-order transition; if $b<0$, a first-order one; if $b=0$, one obtains what is now called a tricritical point. Solving for η one obtains the temperature variation of η.

We now describe the phenomena of SHG and its relation to η. If the electric field E^{ω} of a light beam of frequency ω is intense enough, it creates in a noncentrosymetric crystal a polarization $P^{2\omega}$ at a frequency 2ω given by

$$P_i^{2\omega}=d_{ijk}E_j^{\omega}E_k^{\omega},\quad i,j,k=1\text{ to }3\;, \tag{4}$$

where d_{ijk} is a third-rank tensor such as the piezoelectric tensor. As quartz is nonabsorbing in visible light, the Kleinman rules apply[16] and hence $d_{14}=0$. Thus there is only one coefficient for SHG, d_{11}, which belong to the B_1 representation, and so changes its sign with **Dauphiné** twinning. We have already used this property to make direct optical observations of Dauphiné twins.[27] (As photoelastic constants p_{14} and p_{41} change their sign with Dauphiné twinning, one can observe twins by photoelastic experiments.[21] This also can be done with the electro-optic effect produced[28] by e_{11}.)

So d_{11}, belonging to B_1 representation, is an odd function of η. Furthermore we assume that d_{11} is a linear function of η. With this approximation, by measuring the SHG coefficient we get a direct measurement of the order parameter. The use of

SHG to study structural phase transitions, mainly ferroelectric ones, has been recently reviewed by Vogt.[29]

To summarize this part the α-β transition of quartz can be described by an order parameter η which is a third-order tensor transforming under the symmetry operation of (622) as B_1 representation. The properties which are sensitive to Dauphiné twinning are expressed as odd functions of η. Among them there is the SHG coefficient d_{11}. The properties not changed by Dauphiné twinning are even functions of η. Landau's theory for first-order transition gives the temperature variation of η.

III. EXPERIMENTAL RESULTS

In α-quartz the nonlinear polarization $P_i^{2\omega}$ produced by an electric field E_i is given by

$$\begin{aligned} P_x^{2\omega} &= d_{11}E_x^2 - d_{11}E_y^2 , \\ P_y^{2\omega} &= -2d_{11}E_xE_y , \\ P_z^{2\omega} &= 0 . \end{aligned} \tag{5}$$

This work was carried out using only monodomain samples, so d_{11} is the same everywhere, and we take it to be positive. The second-harmonic (SH) intensity $I_{2\omega}$ produced in a plane parallel slab of thickness l is given by

$$I_{2\omega} \sim \left(\frac{d_{11}\sin\frac{1}{2}|\Delta\vec{k}|l}{|\Delta\vec{k}|} \right)^2 , \tag{6}$$

where $\Delta\vec{k} = \vec{k}_2 - 2\vec{k}_1$, with $\vec{k}_1$ and $\vec{k}_2$ the wave vectors of the fundamental and harmonic light waves. In a crystal such as quartz, without phase-matching directions (i.e., directions where $\Delta\vec{k} = 0$), the usual method to measure d_{11} is to rotate the crystal around some axis, which by changing the magnitude of $|\Delta\vec{k}|$ produces intensity variations, called Maker's fringes,[16] from which one can calculate d_{11}. If the temperature changes, $\Delta\vec{k}$ and l are also temperature dependent and produce Maker's fringes. To make an accurate measurement we built a furnace with a rotating core, so that at each temperature we can obtain Maker's fringes. We use a Quantronix A 112 Nd^{3+} – YAG laser with an acousto-optic Q switch, which produces pulses of 1.06-μm light of 5-kW peak power at 1 kHz. The laser beam is divided in two equal parts. One is used to generate SH in a fixed quartz sample which is used to check the laser intensity while the other one is slightly focussed by a lens of 300-mm focal length. After a laser warm up of half an hour, short-term fluctuations in SH signal intensity are of about $\pm 3\times10^{-2}$. The sample is a slab of $10\times10\times2$ mm with optically polished plane parallel surfaces. It is a BC cut and the crystal normal is rotated from Z by $-31°$ around X.[30] The X axis is vertical and is the rotation axis, so the YZ plane is the incidence plane. Laser light is polarized horizontally, and as quarts is uniaxial it has an extraordinary polarization. In the crystal it produces an ordinary SH beam according to

$$P_x^{2\omega} = -d_{11}E_y^2 . \tag{7}$$

When we change the incidence angle around normal incidence by rotating the sample around X, the extremity of $\vec{k}_1$ describes an ellipse the axes of which are Z and Y; the extremity of $\vec{k}_2$ describes a circle, so that the modules of $\Delta\vec{k}$ varies nearly linearly with the rotation angle, producing nearly equally spaced Maker's fringes. The fringes measured at room temperature for an incidence angle θ going from $-20°$ (on Z side) to $+20°$ (on Y side) are plotted in Fig. 1(a). Fringes obtained at a temperatrue of 0.2 °C below T_t on heating are plotted in Fig. 1(b). At room temperature the width of the fringes varies from 3.3° at about $\theta = +15°$ to 3.0° at about $\theta = -15°$. Our measurements were made mainly around $\theta = +15°$, where the maximum intensity of fringes depends little on θ. Furthermore close to normal incidence there are interferences with reflected fundamental and SH beams which produce small erratic variations. Two fringes are produced on heating from room temperature to T_t. The width of the fringes changes from 3.1° at room temperature to 3.4° near T_t. With heating the SH intensity decreases by nearly one order of magnitude from 20 °C to the transition temperature (Fig. 2). (We have found only a short report[31] in the literature on the temperature variation of SH intensity up to the transition point.) In our experiment there is a sharp discontinuity at about 573.2 °C on heating (we have made no attempt to make absolute temperature measurements; only temperature differences are accurately known). On cooling there is a hysteresis of about 1.5 °C after which the intensity regains the same value as during heating. We check by observation of SH that the crystal remains monodomain in the α-phase.[27] Intensity variations are smooth and reproducible except in a temperature interval of about 0.1 °C below transition temperature (on heating and on cooling). Sometimes just at the transition temperature we observe a spike the intensity of which can reach the value of the SH intensity variation at the transition. This effect may be produced by twinning appearing just at the transition, which is one explanation given by Shapiro et al. for the anomalous light scattering observed at the transition.[13,14] Alternatively, it may be produced by a temperature gradient in the sample causing the passage of a phase front, which we have observed between crossed polarizers. A rough estimation of the temperature gradient in the sample, calculated from radiation loss by the apertures, gives around 10^{-2} °C/mm. The temperature can be regulated to within two or three hundredths of a degree. Most of our results were obtained at a heating or cooling rate of 0.1 °C/min.

Above T_t, in the β-phase, there is a small residual SH signal the intensity of which is about 10^{-4} of the SH intensity in the α-phase just below T_t, i.e., about 10^{-5} of the SH intensity at room temperature. In this paper we describe only SHG in the α-phase. We have made attempts to observe "critical" opalescence[8,13] but they were unsuccessful. This could be related to the fact that our sample was monodomain and remains so even after an excursion of a few degrees into the β-phase.

To obtain d_{11} from the SH intensity measurement we have followed the analysis of Jerphagnon and Kurtz.[32] Taking their formula, with θ the incidence angle, θ_1' and θ_2' the refraction angles for fundamental and SH light, n_1 the extraordinary refractive index for the fundamental, n_2 the ordinary refractive index for the SH light, one has (neglecting small effects related to the finite cross section of the beam)

$$I_{2\omega}=Nd_{11}^2\,t'^4\,T_{2\omega}p^2(\theta)\times(n_1^2-n_2^2)^{-2}\sin^2(\tfrac{1}{2}|\Delta\vec{k}|l)\,E_\omega^4\,, \tag{8}$$

$$t'=\frac{2\cos\theta}{n_1\cos\theta+\cos\theta_1'}\,, \tag{9}$$

$$T_{2\omega}=\frac{2n_2\cos\theta_2'(n_1\cos\theta_1+\cos\theta)\,(n_2\cos\theta_2'+n_1\cos\theta_1')}{(n_2\cos\theta_2'+\cos\theta)^3}\,, \tag{10}$$

$$p=\cos^2(31^\circ-\theta')\ . \tag{11}$$

t' is the linear Fresnel factor for the fundamental, $T_{2\omega}$ a nonlinear Fresnel factor, $p(\theta')$ the projection factor of the electric field E_ω on Y, and N a numerical factor. After $d_{11}(t)$ the main temperature variation of $I_{2\omega}$ for a fixed incidence angle comes from $(n_2^2-n_1^2)^{-2}$. At room temperature the refractive indices are well known[1,3] and there is good agreement between the experimental and theoretical values of Maker's fringes. But the temperature dependence of the refractive indices is not so well known. Values given in Dana's book[1] are those of Rinne and Kolb[33] measured to five significant figures. There is another measurement to 458 °C by Reed[3,34] to six significant figures which differs, at 400 °C for example, by 5×10^{-4} from the values of Rinne and Kolb. Both these measurements were made in the visible spectrum and the extrapolation to 1.06 μm is not very reliable. We can obtain experimentally, however, the temperature variation of $n_2^2-n_1^2$ from the width of Maker's fringes. Using Snell's law

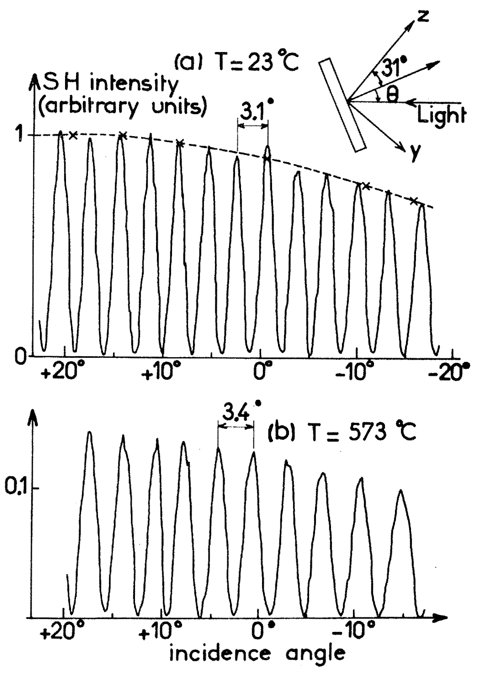

FIG. 1. (a) Variation of second-harmonic intensity when the quartz sample is rotated at room temperature (Maker's fringes). The dashed curve is the calculated envelope of Maker's fringes. (b) Maker's fringes at 573°C (0.2°C below the transition temperature, on heating).

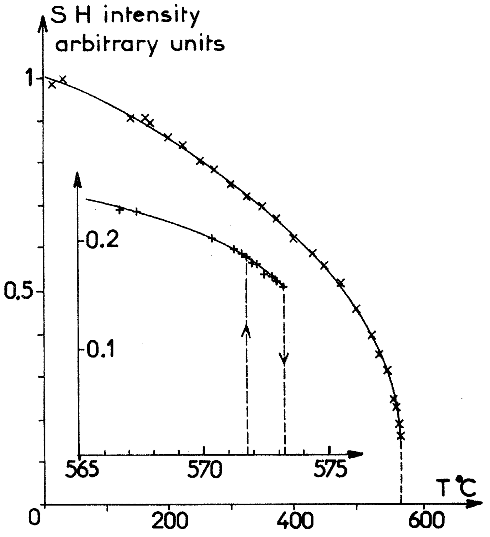

FIG. 2. Variation of the second harmonic intensity (for an incidence angle of +15°) as a function of temperature. The transition region is expanded to show the hysteresis of about 1.5°C.

$$\sin\theta = n_2 \sin\theta_2' = n_1 \sin\theta_1' \,, \tag{12}$$

$$\begin{aligned} n_2^2 - n_1^2 &= n_2^2 \cos^2\theta_2' - n_1^2 \cos^2\theta_1' \\ &= (n_2 \cos\theta_2' - n_1 \cos\theta_1')(n_2 \cos\theta_2' + n_1 \cos\theta_1') \,, \end{aligned} \tag{13}$$

$$\begin{aligned} |\Delta\vec{k}| &= (n_2 \cos\theta_2' - n_1 \cos\theta_1')(\pi/\lambda_2) \\ &= \Delta n_\perp (\pi/\lambda_2) \,, \end{aligned} \tag{14}$$

where λ_2 is the SH wavelength in vacuum.

Using the known value of thermal expansion of quartz we found from the temperature variation of Maker's fringes that $\Delta n_\perp$ varies between 115.4×10^{-4} at 23 °C and 120.4×10^{-4} at T_t with an absolute error of about 10^{-4}. These results are in better agreement with the values calculated from the data of Reed than from that of Rinne and Kolb. The remaining factors in Eq. (8) depend only on the values of refractive indexes and not on their differences. So here we can take the values of Rinne and Kolb, which go up to T_t. With these data the temperature variation of the product of all these factors is 10^{-2} from 23 to 573 °C. We have not tried to calculate the δ_{11} of Miller,[35] which seems to be a more basic quantity than d_{11} because here also one needs accurate values for the temperature dependence of the refractive indexes. Thus from our SH measurement we have obtained the values of d_{11} and hence of η (assuming a linear relation) as a function of temperature shown in Table I, with a relative accuracy of about $\pm3\times10^{-2}$. We have normalized to the value 1 at 23 °C [the value of d_{11} of quartz relative to the nonlinear susceptibility of potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) is given by Jerphagnon and Kurtz[36]]. At the transition $\eta = 0.384$ which is not small, and hence the transition is clearly first order. In Sec. IV our results are compared with Landau's theory and with other experimental results.

TABLE I. Values of the order parameter η, normalized to 1 at 23 °C as a function of temperature, obtained from our SHG measurement of d_{11} assuming that $\eta = d_{11}$.

t (°C)	η	t (°C)	η	t (°C)	η
23	1.000	452	0.726	566.55	0.463
51	0.987	477	0.698	567.23	0.460
144	0.939	502	0.656	570.25	0.434
177	0.930	505	0.649	571.15	0.423
202	0.911	510	0.642	0.45	0.419
227	0.900	520	0.617	0.67	0.415
252	0.877	528	0.611	0.90	0.409
277	0.867	530	0.602	572.05	0.408
302	0.845	539	0.574	0.10	0.406
327	0.829	550	0.548	0.42	0.399
352	0.816	552	0.542	0.67	0.395
377	0.797	553	0.531	0.92	0.389
402	0.768	562	0.488	573.18	0.384
432	0.748	564.6	0.480		

IV. DISCUSSION OF EXPERIMENTAL RESULTS

Much work has been done recently on phase transitions,[37,38] most of this on second-order transitions. It has been shown both theoretically and experimentally that the classical mean field theory is inaccurate near the critical temperature, and that several critical exponents are necessary to describe these transitions. Less attention has been paid to first-order transitions. However there is a revival of interest mainly produced by the discussion of tricritical points[39] on the borderline between first- and second-order transitions.

A. Application of Landau's theory

First we compare our results for $\eta(t)$ to the Landau theory. Taking terms up to the sixth power in F we obtain for η in the α-phase from Eq. (3),

$$\eta^2 = \{-b + [b^2 - 4(t-t_0)c]^{1/2}\}/2c \,, \tag{15}$$

the inverse function of which is

$$t = t_0 - (b\eta^2 + c\eta^4) \,. \tag{16}$$

Equation (15) can be also written

$$\eta^2 = \eta_1^2 \left[1 + \left(1 - \frac{t-t_0}{t_1-t_0}\right)^{1/2}\right], \tag{17}$$

with $t_1 = t_0 + b^2/4c$ and $\eta_1^2 = -b/2c$. t_0 is the lower existence temperature of the β phase, t_1 is the upper existence temperature of the α-phase, η_1 is the minimum value of the order parameter in the α-phase, obtained at temperature t_1. The temperature of thermodynamic equilibrium between the two phases is $t_c = t_0 + \frac{3}{4}(t_1 - t_0)$.

We seek a least-squares fit of our experimental value for η according to Eq. (15) taking several ranges of temperature. The results of these fits are given in Table II. The fit is good in all temperature ranges giving a mean square deviation σ of 3×10^{-3} which is better than the experimental accuracy. In Figs. 3(a) and 3(b) the curve of the fit obtained on the whole temperature range is plotted with the experimental η values. The deviation between experimental and theoretical values is also plotted. There are nearly no systematic deviations.

There is, however, an inconsistency in the fit with Landau's formula. The calculated temperature of coexistence t_c is 571.54 °C. But experimentally a hysteresis region is found between 571.7 and 573.2 °C and so the calculated t_c is outside the experimental hysteresis temperature range. We think that as the fit is made only with values of η measured in the α-phase it gives a good representation of this phase, and only a poor representation of the β-phase, so it is not adequate for determining t_c and the hysteresis region. The value of $t_1 - t_0$ of about 9.5 ℃ we obtain is in agreement with that of Axe and Shirane[18] deduced from their neutron measurements. Grimm and Dorner have recently used Landau's formula to interpret structural and thermal expansion data which however are not sufficiently accurate to give an unambiguous fit.[19]

B. Comparison of SHG with other physical properties

In the following comparisons we have made translations of temperature scales to get the same transition temperature, and normalized the value of the experimental result to 1 at 23 ℃ or 0 ℃ (except for C_{14}). Previously Mayer[40] had also obtained an empirical temperature-dependent order parameter from his elastic constant measurement without using Landau's theory.

1. *Optical properties*

Some optical properties such as the SHG coefficient d_{11}, the electro-optic coefficient e_{11}, and elasto-optic effects from p_{14} and p_{41} vary as η. The others vary as η^2. Refractive indexes are not well-known in particular near T_t. There exist, however, better measurements of the birefringence Δn. We use the data of Wright and Larsen[41] measured with Na light on heating. But only one part $\Delta n'$ of the birefringence is connected with the order parameter. For the birefringence we tried the simplest approximation. We subtract from $\Delta n(t)$ a constant, the value of Δn in β phase just above T_t:

$$\Delta n'(t) = \Delta n(t) - \Delta n(T_t^+) .$$

TABLE II. Parameter values obtained for three fits of experimental η values to the formula $t = t_0 - b\eta^2 - c\eta^4$, t_i and t_f are the lower and upper temperatures used for the fit, t_0 is the lowest calculated existence temperature of β phase, t_1 is the highest calculated existence temperature of α phase, η_1 is the value of η for temperature t_1 and σ the mean-square deviation between experimental and theoretical values.

	I	II	III
from t_i (°C)	23	520	550
to t_f (°C)	573.18	573.18	573.18
t_0 (°C)	564.37	563.36	564.31
t_1 (°C)	573.94	573.78	573.90
$-b$	166.8	176.5	166.2
$+c$	726.6	747.7	720.1
η_1	0.3388	0.3436	0.3397
$10^3\sigma$	3.0	2.7	2.4

In Figs. 3(a) and 3(b) is plotted $[\Delta n'(t)]^{1/2}$, which should vary as η, normalized to 1 at 23 ℃. The agreement with the variation of η is surprisingly good. The greatest relative diffrence is less than 1.5×10^{-2} at about 300 °C. Near T_t the difference

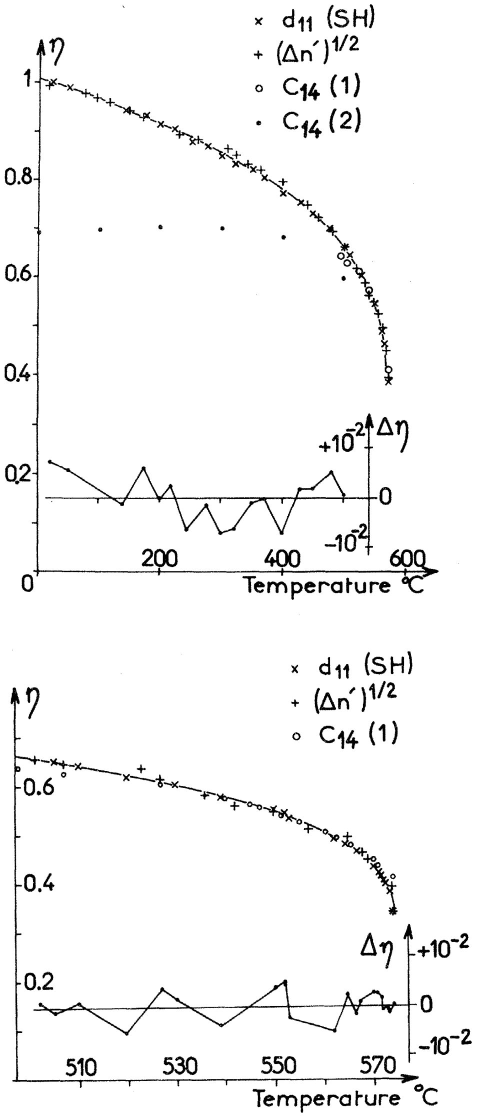

FIG. 3. (a) Plot of the order parameter η obtained from our second-harmonic measurement as a function of temperature (η is normalized to 1 at 23°C). The curve is the best fit to Landau theory in the (23–573.18)°C temperature range. Also plotted is the square root of the anomalous component of the birefringence $\Delta n'$ and the measurements of C_{14} (1) by Höchli and C_{14} (2) by Hatanasoff and Hart. The deviation $\Delta\eta$ (magnified 10 times) between our experimental points and the curve of the fit is plotted in the lower part. (b) Same as (a) for the (500–573.18)°C temperature range. The full curve is the best Landau fit for the (23–573.18)°C temperature range.

is less than the relative uncertainty (5×10^{-2}) in Δn. This agreement between the two sets of measurements over such a large temperature range must be a little furtuitous. The temperature dependence of the rotatory power is also known and varies roughly as $\eta^2(t)$ in the α-phase. But the experimental data[3] are not as accurate as the birefringence measurements and comparison is not very meaningful.

2. *Thermal expansion*

The expansions parallel and perpendicular to the optical axis, which are nearly proportional,[12] may vary with temperature as η^2. In addition there can be a normal expansion linear with temperature. There also we have tried the approximation of a temperature-independent baseline equal to the expansion value in the β phase just above T_t. The values for $L_x(T_t^+) - L_x(t)$ from the results of Mayer,[40] Sosman,[3] Jay,[42] and Berger *et al.*[43] are plotted in Fig. 4 with the $\eta^2(t)$ curve obtained from the fit of our experimental points to Landau's theory. The agreement is not as good as for birefringence. But the deviation from $\eta^2(t)$ curve is of the same order as the differences among the various dilatometric data themselves. The results for L_z are the same as for L_x and are not plotted. One would need very accurate expansivity measurements to improve these results. As the total expansion between 20 °C and T_t is about 10^{-2}, and the discontinuity at the transition about 10^{-3}, one needs expansivity measurements with a resolution of 10^{-5} at 570 °C to make a meaningful comparison with other measurements.

3. *Piezoelectric and elastic constant*

The temperature variation of the piezoelectric constant a_{11} has been measured by Cook and Weissler.[44] They found that $a_{11}(573\ °\mathrm{C})/a_{11}(20\ °\mathrm{C}) = 0.54$, i.e., greater than the same ratio for d_{11}. The measurement of a piezoelectric constant is quite difficult, depending on the values of the elastic constants which also are anomalous near T_c. New measurements of a_{11} would be interesting [such measurements have been made recently on NH_4Cl (Ref. 45) where the piezoelectric constant is also linearly related to the order parameter].

In comparing elastic constants with thermodynamic data one must use the isothermal values, but experimental measurements generally use dynamic methods which give adiabatic values. In general the difference is small but in quartz near the transition, this difference can increase up to (10–20)%.[12] As the difference depends on the specific heat, which is known rather inaccurately, it is difficult to make corrections. In the following we will deal only with adiabatic values, and so there may be systematic differences.

Among the elastic constants one can separate three groups. Those such as C_{14} which vary as η; C_{44}, C_{66} which vary as η^2; and $C_{11}, C_{12}, C_{33}, C_{13}$, which have anomalies in the α and β phase. In this last case, there is a great anharmonic coupling with fluctuations. In addition we have no indication of the value of the normal part of these elastic constants: therefore we have not tried to use them for comparisons. In Fig. 4 is plotted $C'_{66}(t) = C_{66}(t) - C_{66}(T_t^+)$ obtained from the measurements of Hatanasoff and Hart.[46] This differs slightly from our result for $\eta^2(t)$, but it is within the experimental accuracy. Other measurements of $C_{66}(t)$ by Zubov and Firsova[47] are in agreement except close to T_t where the discontinuity is four times smaller. For C_{44} the two sets of data are not in good agreement.

Höchli has recently made a new measurement of temperature variation of C_{14},[15] also shown in Figs. 3(a) and 3(b). The magnitude of C_{14} has been adjusted at 550 °C. His data are in good agreement with our results, except for his highest temperature point, which is in the hysteresis region, and for the two lowest temperature points near 500 °C. The measurement of C_{14} by Hatanasoff and Hart[46] is also shown in Fig. 3(a), which indicates that C_{14} saturates and has a smooth maximum around 200 °C. Since a normal order parameter increases as the temperature tends to 0 °K with an horizontal tangent there, C_{14} cannot be linearly related to the order parameter on all the temperature range.

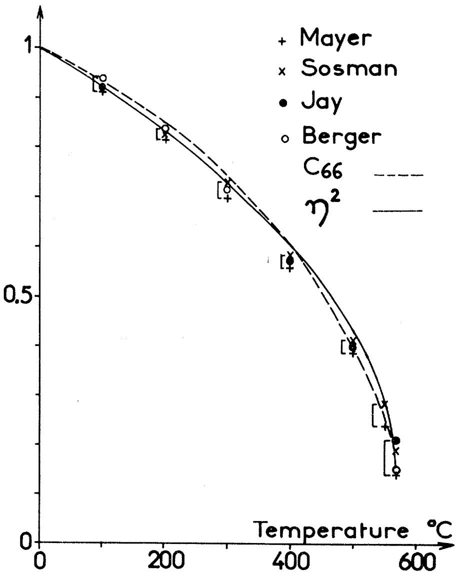

FIG. 4. Comparison of $\eta^2(t)$ (full curve) obtained from our data with other physical properties; expansion perpendicular to optical axis measured by various authors and elastic constant C_{66} (dashed curve).

Near 500 °C Höchli's results are not in agreement with those of Hatanasoff and Hart, but they agree with those of Zubov and Firsova.[47]

Höchli and Scott[48] have interpreted the C_{14} measurements, as well as the soft-mode frequency and structural data, by introducing a formula with a critical exponent of $\frac{1}{3}$. We discuss this interpretation in Sec. V.

V. CRITICAL EXPONENT FOR A FIRST-ORDER TRANSITION

For a second-order transition the order parameter η has a temperature dependence, close to the transition temperature t^*, given by[38]

$$\eta = C(t^* - t)^\beta . \qquad (18)$$

In many substances $\beta = \frac{1}{3}$. To take into account the discontinuity in a first-order transition, Höchli and Scott[48] have proposed the formula

$$\eta = \eta^* + C(t^* - t)^\beta , \qquad (19)$$

and they have found $\beta = \frac{1}{3}$ in fitting the C_{14} data.

They give no real justification for (19) except by analogy with Landau's result for a first-order transition (where $\beta = \frac{1}{2}$) close to the stability limit. As shown in Sec. IV their C_{14} data also agree quite well with the Landau formula obtained from our experiment and so we investigate this question of fitting in greater detail. Firstly, we tried to fit our data for η (from our SHG measurement) to Eq. (19). The results for this four-parameter fit are given in Table III. The best fit, with the four parameters free gives a value of β very near $\frac{1}{3}$, and if we take $\beta = \frac{1}{3}$ with the three other parameters free we get a fit which represents our data as well as Landau's formula. The deviations between the two fits [the one with Landau's theory and the other with Eq. (19) taking $\beta = \frac{1}{3}$] are plotted in Fig. 5. These deviations are less than 5×10^{-3} (so better than our experimental uncertainty) over the whole temperature range from 23 to 573.2 °C. If we vary β, the values of other parameters obtained in the fit vary as a function of β, the mean square deviation increasing smoothly. However for $1/\beta > 4.88$ the discontinuity η^* at the transition becomes negative, which has little physical sense.

TABLE III. Least-square fit obtained for our measurements of η with a four-parameter formula, $\eta = \eta^* + C(t - t^*)^\beta$, σ is the mean-square deviation. (f) following a number indicates that this value was kept fixed for the fitting procedure.

Fitted $t = 23$ to 573.18 °C						
$1/\beta$	3 (f)	3.06	4 (f)	4.88	6 (f)	
t^* (°C)	572.11	572.28	575.10	577.6	579.6	
η^*	0.299	0.291	0.147	0 (f)	−0.182	
C	0.0852	0.0896	0.1734	0.270	0.405	
$10^3\sigma$	3.3	3.3	5.1	6.5	7.6	
Fitted from $t = 520$ to 573.18 °C						
$1/\beta$	2 (f)	2.89	3 (f)	6 (f)	6.11	6 (f)
t^* (°C)	571.24	572.11	572.24	574.29	574.38	574.56
η^*	0.371	0.306	0.296	0.0125	0 (f)	0 (f)
C	0.0351	0.079	0.086	0.310	0.320	0.316
$10^3\sigma$	4.1	2.7	2.7	3.1	3.1	3.2

If we decrease the temperature range used for fitting, the results for a four-parameter fit become ambiguous. For $t = 520$ to 573.18 °C, $1/\beta$ can vary from nearly 2 to 6 without changing significantly the mean square deviation σ (Table III). On a small temperature range, as Burns and Scott[49] have already shown, a four-parameter least-squares fit is very insensitive to the value of the exponent. Thus one can fix the exponent with some latitude, and obtain a good fit. As the temperature range increases the exponent is more well defined; however it is not expected that a critical formula such as Eq. (18) or (19) is valid over a great temperature range Δt (the $\Delta t / t^*$ found for the critical region in a structural second-order phase transition is typically[50] 5×10^{-2}). We have also tried a three-parameter fit, putting $\eta^* = 0$. There is no good fit from 20 to 573.18 °C. But between 520 and 573.18 °C we find $\beta = \frac{1}{6}$. (Such an exponent is in agreement with the results of Banda *et al.*[51] as reported by Scott.[5])

To summarize, in a temperature range of 20 to 573.18 °C, our data fit equally well Landau's theory

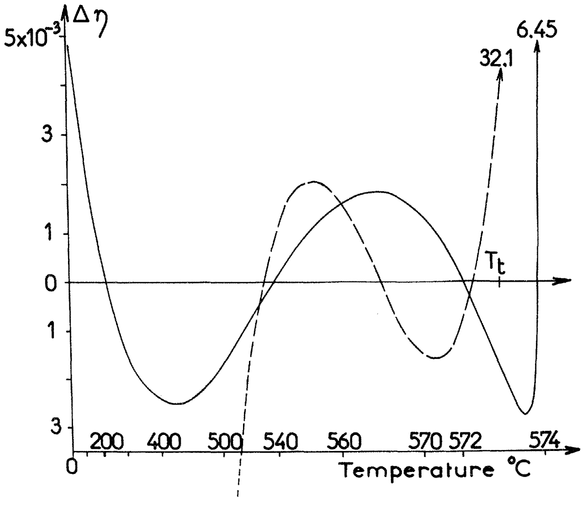

FIG. 5. Deviation $\Delta\eta$ between the least-square fits using, respectively, the Landau theory and a formula with a critical exponent β. Full line = $\beta = \frac{1}{3}$; the other parameters are determined by fitting the experimental points on the (23°–573.18)°C temperature range. Dashed line = $\beta = \frac{1}{6}$ ($\eta^* = 0$) with a fit on the (520 –573.18)°C temperature range. Temperatures are plotted on a logarithmic scale for clarity.

and Eq. (19), with $\beta = \frac{1}{3}$. In the reduced range of 520 to 573.18 °C a four-parameter fit is ambiguous but we can also find $\beta = \frac{1}{3}$. A three-parameter fit with $\eta^* = 0$ is also possible, and then we find $\beta = \frac{1}{6}$. One can ask if the similarities between Landau's theory and formulas with critical exponents such as (19) are fortuitous or if there is a fixed relation between them. By changing η and t units so that $\eta_1 = 1$ and $t_1 - t_0 = 1$ in Landau's formula [Eq. (17)] and choosing the origin of temperature scale at t_0, (17) takes the reduced form

$$\eta^2 = 1 + (1-t)^{1/2} \tag{20}$$

or

$$t = +2\eta^2 - \eta^4 . \tag{21}$$

Equation (19) can also be written

$$t = t^* + k(\eta - \eta^*)^{1/\beta}, \quad \text{with } k = -(1/c)^{1/\beta} . \tag{22}$$

As there are four parameters, there exists a point on the abscissa η where t and its first three derivatives are equal in the two curves. Solving these four equations we obtain

$$\begin{aligned} &\beta = (1+3\eta^4)/(2-6\eta^2+12\eta^4), \\ &\eta^* = 4\eta^3/(1+3\eta^4) \\ &k = \beta(4\eta - 4\eta^3)/(\eta-\eta^*)^{-1+1/\beta}, \\ &t^* = 2\eta^2 - \eta^4 - k(\eta-\eta^*)^{1/\beta} . \end{aligned} \tag{23}$$

The variation of these parameters as a function of η are given in Table IV. One sees that for $\eta = (1+2/\sqrt{3})^{1/2}$ and $t = -\frac{1}{3}$ one gets $\beta = \frac{1}{3}$. We can also initially fix $\eta^* = 0$; three parameters remain, and so we can equate t and its first two derivatives. On solving these three equations we obtain

$$\begin{aligned} &\beta = \frac{\eta^2 - 1}{4\eta^2 - 2}, \quad t^* = \frac{\eta^4}{\eta^2 - 1}, \\ &k = \beta(4\eta - 4\eta^3)/\eta^{-1+1/\beta} . \end{aligned} \tag{24}$$

The variation of these parameters as a function of η are also given in Table IV. For $\eta = \sqrt{2}$ and $t = 0$ we have $\beta = \frac{1}{6}$. The curves corresponding to these fits for $\beta = \frac{1}{3}$ and $\beta = \frac{1}{6}$ are given in Fig. 6 with their differences from Landau's curve [Eq. (20)]. The values of the reduced parameters for which the relative difference $\Delta\eta/\eta$ between Landau's curve and the curves with $\beta = \frac{1}{3}$ and $\beta = \frac{1}{6}$ is equal to 10^{-3} and 10^{-2} are given in Table V. For quartz the value of t given here must be multiplied by 9.5 °C to obtain the real temperature scale. With a multiparameter fit the different curves lie even closer. One sees on Fig. 5 that the curve for a four parameter fit with $\beta = \frac{1}{3}$ crosses the Landau curve at four points as expected and that the curve for a three-parameters fit ($\beta = \frac{1}{6}$, $\eta^* = 0$) crosses at three points. One can even fit with a two-parameter curve, imposing for example $\beta = \frac{1}{3}$ and $\eta^* = 0$, which will be valid only in a smaller temperature range. However, if the data are not very accurate, one can find that this fit is acceptable, even in a larger temperature range.

Conversely, a Landau curve can be found very close to a critical one. But as long as there is

TABLE IV. Values found for the parameters of the formula $t = t^* + k(\eta - \eta^*)^{1/\beta}$ taking the best contact with Landau formula $t = 2\eta^2 - \eta^4$ at a point of coordinates (t, η).

Four parameters

η	t	$1/\beta$	k	t^*	η^*
$+\infty$	$-\infty$	4	-1	$+\infty$	0
3	-63	3.77	-1.88	2.11	0.44
2	-8	3.47	-3.32	1.32	0.653
$(1+2\sqrt{3})^{1/2}$	-0.33	3	-5.87	1.07	0.847
1.2	0.81	2.53	-7.26	1.01	0.96
1	1	2	-4	1	1

Three parameters

η	t	$1/\beta$	k	t^*
$+\infty$	$-\infty$	4	-1	$+\infty$
3	-63	4.25	-0.64	4.8
2	-8	4.67	-0.41	2.29
$\sqrt{2}$	0	6	-0.167	1.33
1.2	0.81	8.54	-0.06	1.10
1	1	$+\infty$	0	1

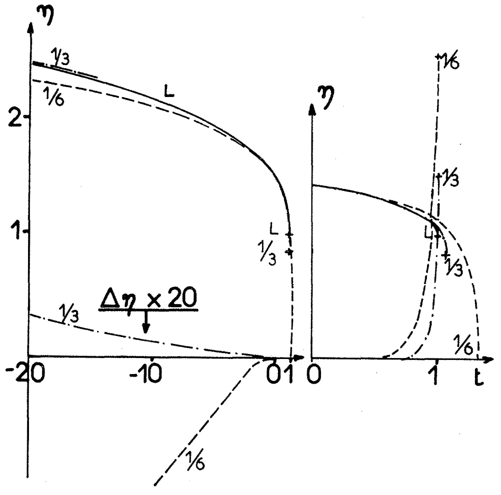

FIG. 6. Plot of the reduced Landau formula $\eta^2 = 1 + (1-t)^{1/2}$ and of curves with critical exponent $\beta = \frac{1}{3}$ and $\beta = \frac{1}{6}$ ($\eta^* = 0$). The differences between these curves and that of Landau magnified 20 times are also plotted. The temperature scale has been changed in the figure on the right.

no model or theory to support a formula such as (19) it seems better to accept Landau's formula, which can be obtained from very simple hypotheses. It is also possible that the range of validity of the Landau theory is greater for a first-order transition than for a second-order transition, where fluctuations diverge. Thus for a first-order transition one must be careful in introducing a formula with critical exponents. A multiparameter fit has often enough freedom to fit experimental data, which always have some dispersion. The more accurate the data, the more unambiguous the fit is. In the case of quartz, vary accurate data are required to show deviation from Landau's theory of the order parameter. However Landau's theory cannot explain all the phenomena at the transition, such as the anomalous increase of the specific heat or the variation of elastic constant in the β phase, which are in some way related to fluctuations.

TABLE V. Values of t and η in reduced coordinates for which the relative difference $\Delta\eta/\eta$ between Landau's formula and a critical exponent formula with four parameters ($\beta = \frac{1}{3}$) and with three parameters ($\beta = \frac{1}{6}$ and $\eta^* = 0$) is 0, $\pm 10^{-3}$, and $\pm 10^{-2}$. (To apply these results to quartz multiply t by 9.5 °C.)

$\left\lvert\frac{\Delta\eta}{\eta}\right\rvert$	10^{-2}	10^{-3}	0	10^{-3}	10^{-2}
		Four parameters			
η	2.53	1.91	1.468	1.23	1.12
t	−28.3	−6.0	−0.33	0.73	0.94
		Three parameters			
η	1.81	1.56	1.414	1.3	1.20
t	−4.15	−1.1	0	0.52	0.81

VI. CONCLUSION

In this paper we have introduced an order parameter η, following Landau's theory which describes the α-β transition of quartz. We show that assuming a linear relation between η and the SHG coefficient d_{11}, one can obtain the temperature variation of η by a measurement of the SH intensity. We show that with an accuracy better than the experimental error the anomalous part of the birefringence is proportional to η^2 from room temperature to the transition temperature. This relation also holds, but less accurately, for thermal expansion and for the elastic constant C_{66}. There is also a linear relation between η and C_{14} but only from 520 °C to the transition temperature of 573.2 °C. We find that for quartz $\eta(t)$ is well represented by a formula deduced from Landau's theory. Our experimental data can also be fitted to a critical curve with a power $\frac{1}{3}$ on all the temperature range, or with a power $\frac{1}{6}$ near the transition temperature. These values of critical exponents can be obtained in a straightforward way by fitting curves with power law to Landau's curve. So the fact that one can represent experimental data for a first-order transition, with critical exponent formula is not evidence of critical behavior. Deviation from Landau's (or mean-field theory) can be obtained only with accurate data, showing systematic difference from classical theory greater than the experimental uncertainty.

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[1] C. Frondel, *Dana's System of Mineralogy,* 7th ed. (Wiley, New York, 1962), Vol. III.

[2] Le Chatelier, C. R. Acad. Sci. (Paris) 108, 1046 (1889).

[3] R. B. Sosman, *The Properties of Silica* (Chemical Catalogue Co., New York, 1927).

[4] R. B. Sosman, *The Phases of Silica* (Rutgers U. P., New Brunswick, N. J., 1965).

[5] J. F. Scott, Rev. Mod. Phys. 46, 83 (1974).

[6] M. L. Keith and O. F. Tuttle, Am. J. Sci. Vol., 203 (1952).

[7] N. N. Sinel'nikov, Dokl. Akad. Nauk SSSR 92, 369 (1953).

[8] I. A. Yakolev, T. S. Velichkina, and L. F. Mikheeva, Dokl. Akad. Nauk SSSR 106, 675 (1956); Kristallografiya 1, 91 (1956).

[9] I. A. Yakolev and T. S. Velichkina, Usp. Fiz. Nauk 63, 411 (1957).

[10] L. H. Cohen and W. K. Klement Jr., J. Geophys. Res. 72, 4245 (1967).

[11] W. K. Klement Jr. and L. H. Cohen, J. Geophys. Res. 73, 2249 (1968).

[12] R. S. Coe and M. S. Paterson, J. Geophys. Res. 74, 4921 (1969).

[13] S. M. Shapiro and H. Z. Cummins, Phys. Rev. Lett. 21, 1578 (1968).

[14] S. M. Shapiro, Thesis (1969) unpublished.

[15] U. T. Höchli, Solid State Commun. 8, 1487 (1970).

[16] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1966).

[17] R. A. Young (unpublished).

[18] J. D. Axe and G. Shirane, Phys. Rev. B 1, 342 (1970).

[19] H. Grimm and B. Dorner, J. Chem. Phys. Solids (to be published).

[20] L. Landau and E. Lifchitz, *Physique Statistique* (Edition de Moscou, 1967).

[21] K. Aizu, J. Phys. Soc. Japan 34, 121 (1973).

[22] W. Cochran, Adv. Phys. 18, 157 (1969).

[23] P. B. Miller and J. D. Axe, Phys. Rev. 163, 924 (1967).

[24] V. K. Semenchenko and V. B. Oshokova, Izv. Akad. Nauk SSSR, Neorg. Mater. 55, 766 (1969).

[25] A. G. McLellan, Philos, Mag. 28, 1077 (1973).

[26] V. L. Ginzburg, Sov. Phys.-Usp 5, 649 (1963), and references cited therein.

[27] G. Dolino, J. P. Bachheimer, and M. Vallade, Appl. Phys. Lett. 22, 623 (1973).

[28] G. Dolino (unpublished).

[29] H. Vogt, J. Appl. Phys. 5, 85 (1974).

[30] A mistake was made in Ref. 27. The sample used here had the same BC cut with an angle of normal from Z of −31° (and not 59°).

[31] K. Murayama and K. Kubota, Jpn. J. Appl. Phys. 10, 657 (1971).

[32] J. Jerphagnon and S. K. Kurtz, J. Appl. Phys. 41, 1667 (1970).

[33] F. Rinne and R. Kolb, Neues Jahrb. Mineral. 2, 138 (1910).

[34] J. O. Reed, Ann. Phys. Chem. 65, 707 (1898).

[35] R. C. Miller, Appl. Phys. Lett. 5, 17 (1964).

[36] J. Jerphagnon and S. K. Kurtz, Phys. Rev. B 1, 1739 (1970).

[37] H. E. Stanley, *Introduction to Phase Transition and Critical Phenomena* (Clarendon Press, Oxford, 1971).

[38] T. Riste, *Anharmonic Lattices, Structural Transition and Melting* (Noordhoff, Leiden, 1974).

[39] R. B. Griffiths, Phys. Rev. Lett. 24, 715 (1970).

[40] G. Mayer, Rap. C. E. A. (France) 1330 (1960).

[41] F. E. Wright and E. S. Larsen, Am. J. Sci. 27, 421 (1909).

[42] A. H. Jay, Proc. R. Soc. London A 142, 237 (1933).

[43] C. Berger, L. Eyraud, M. Richard, and R. Riviere, Bull. Soc. Chim. 628 (1966).

[44] R. K. Cook and P. G. Weissler, Phys. Rev. 80, 712 (1950).

[45] E. Mahler and R. Pitka, Solid State Commun. 14, 791 (1974).

[46] J. V. Hatanasoff and P. J. Hart, Phys. Rev. 59, 85 (1941).

[47] V. G. Zubov and M. M. Firsova, Kristallografiya 7, 469 (1962) [Sov. Phys.-Crystallogr. 7, 374 (1962)].

[48] U. T. Höchli and J. F. Scott, Phys. Rev. Lett. 26, 1627 (1971).

[49] G. Burns and B. A. Scott, Phys. Rev. B 7, 3088 (1973).

[50] H. E. Stanley, *Cooperative Phenomena near Phase Transitions* (MIT Press, Cambridge, Mass., 1973).

[51] E. J. Banda, R. A. Craven, P. M. Horn, and M. Blume (unpublished).