the density variation of the band structure into account.

The present theoretical study was motivated by Donovan and Spicer's striking experimental results.[1] The authors are grateful to Mr. T. L. Donovan and Professor W. E. Spicer for bringing these results to their attention, and for many stimulating discussions.

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[1] T. M. Donovan and W. E. Spicer, preceding Letter [Phys. Rev. Letters 21, 1572 (1968)].

[2] W. E. Spicer and R. C. Eden, in Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow, U.S.S.R., 1968 (to be published). This paper contains an extensive list of references to photoemission experiments.

[3] A. I. Gubanov, Quantum Electron Theory of Amorphous Conductors (Consultants Bureau, New York, 1965).

[4] J. Tauc, in "Optical Properties of Solids," edited by F. Abeles (North-Holland Publishing Co., Amsterdam, The Netherlands, to be published). See also J. Tauc, Materials Res. Bull. 3, 13 (1968).

[5] J. Tauc, A. Abraham, L. Pajasova, R. Grigorovici, and A. Vancu, in Proceedings of the Conference on Noncrystalline Solids, Delft, The Netherlands, 1964 (North-Holland Publishing Co., Amsterdam, The Netherlands, 1965), p. 606. See also J. Tauc and A. Abraham, to be published.

[6] H. Richter and G. Breitling, Z. Naturforsch. 13a, 988 (1958).

[7] R. Grigorovici, Materials Res. Bull. 3, 13 (1968).

[8] A. H. Clark, Phys. Rev. 154, 750 (1967).

[9] F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, in Quantum Theory of Atoms, Molecules, and the Solid State, edited by P. O. Löwdin (Academic Press, Inc., New York, 1966), p. 381. See also F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, J. Phys. Soc. Japan Suppl. 21, 7 (1966).

[10] The pseudopotential coefficients used in constructing Fig. 2 are as follows: $v(111) = -0.2497$, $v(220) = 0.0145$, and $v(311) = 0.0115$ (Rydberg units). Also, $(m^*)^{-1} = 0.9924$. See F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, Rhode Island, 1967, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 503, for further details concerning the analogous calculation for normal ($a/a_0 = 1$) germanium.

[11] S. Groves and W. Paul, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod, Paris, France, 1964), p. 41.

[12] Herman, Kortum, Kuglin, and Shay, Ref. 10.

[13] On the other hand, the broad maximum in the photoconductivity spectrum of amorphous germanium observed at 1.1 to 1.2 eV by Grigorovici (Ref. 7) over a wide temperature range [and at 1.5 eV by Clark (Ref. 8) at 4.2°K] may possibly be related to the Λ-type transitions that are responsible for the 1.2 eV peak in the direct transition ϵ_2 calculation for dilated germanium [cf. Fig. 3(a)]. If so, the lower energy optical transitions would be better described by the direct-transition model, and the higher energy transitions by the nondirect-transition model.

CRITICAL OPALESCENCE IN QUARTZ*

S. M. Shapiro and H. Z. Cummins
Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218

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The intense scattering of light by quartz in the vicinity of the α-β transition, first observed by Iakovlev and co-workers in 1955, has been studied by Raman and Brillouin spectroscopy and by visual observation. Our results indicate that the observed "opalescence" does not originate from critical fluctuations of the order parameter but is generated by essentially static domain walls separating microdomains of opposite electrical twins.

Crystalline quartz undergoes a transition at 573°C from the low-temperature α phase (symmetry D_3) to the high-temperature β phase (symmetry D_6). The transition is marked by anomalies in many of the physical properties of quartz.[1] In 1956, Iakovlev, Velichkina, and Mikheeva observed that the scattering of Hg light by quartz increases in the vicinity of the transition by $\sim 10^4$ over the room-temperature level and that under white-light illumination, the scattering volume appears as a "fog zone."[2] They termed this phenomenon "critical opalescence" since it resembles the intense scattering observed in fluids near the critical point. Subsequently Ginzburg and Levanyuk[3] applied Landau's theory of second-order phase transitions and thermodynamic fluctuation theory, and computed the theoretical increase in scattered light at the transition temperature which agreed remarkably well with the experiment. It has since been generally accepted that the intense scattering in quartz at the α-β transition arises from the diverging fluctuations in the order parameter.[4]

Ginzburg also emphasized the dynamical origin of the "opalescence." Taking the order parameter η as the displacement of a silicon atom from its β-phase equilibrium position, the fluctuation in η will then correspond to relative displacements of crystal sublattices so that η is to be identified with one of the zone-center optical lattice vibrations. On the basis of available temperature-dependent spectroscopic information,[5] Ginzburg identified η with the totally symmetric A_1 optical mode whose room-temperature frequency is 207 cm^{-1}. (This identification has been justified by Kleinman and Spitzer's valence-force-model calculations of the atomic motions associated with this mode.[6]) Ginzburg proposed that as the temperature is raised towards the transition temperature T_C, the frequency of this mode should decrease steadily towards zero. The Stokes and anti-Stokes components of the Raman spectrum would approach each other, finally merging into a single quasielastic peak which would continue to narrow, and would grow more intense due to the diverging fluctuations. He suggested that this phenomenon be studied through spectroscopic analysis of the scattered light.

In this Letter we report a series of spectroscopic observations of light scattered by quartz in the vicinity of the α-β transition. In our experiments, natural quartz crystals were slowly heated and cooled through the transition region. The moving zone of intense scattering which Iakovlev, Velichkina, and Mikheeva had reported was also observed in these experiments.

Raman experiments. – In a previous paper we reported temperature-dependent Raman experiments on quartz.[7] We showed that it is not the 207-cm^{-1} line but a small A_1 satellite (at 147 cm^{-1} at room temperature) whose frequency approaches zero at $T \to T_C$. The probable origin of this complication has been discussed recently by Scott[8] in terms of anharmonic coupling between one- and two-phonon excitations. Scott's results imply that at room temperature the 207-cm^{-1} line is essentially a zone-center A_1 optical vibration as had been assumed, while the feature at 147 cm^{-1} is a two-phonon zone-edge excitation. As the temperature is raised, the two excitations become mixed due to the coupling produced by anharmonicity. Around 300°C the excitations are thoroughly mixed and the observed spectral features can no longer be described as one- or two-phonon processes. As T approaches T_C, the excitations again become distinct, and the low-frequency component has become the one-phonon mode. Thus, apart from the complications produced by the hybridization, the earlier assertion that it is the 207-cm^{-1} mode whose frequency approaches zero at the transition is apparently correct.

We have repeated our temperature-dependent Raman measurements of quartz in the vicinity of T_C with the apparatus used in Ref. 7, but with an 800-mW Spectra-Physics argon-ion laser as the Raman source. We find that the frequency of the "soft mode" decreases to ~30 cm^{-1} at 573.4°C at which point it disappears from our spectra. On cooling, it reappears at 572.4°C, one degree below the temperature at which it disappears on heating. The "soft" component is quite broad (>20 cm^{-1}) when it attains its minimum frequency of 30 cm^{-1}. The intense Rayleigh scattering suddenly appears with the disappearance (on heating) and reappearance (on cooling) of the Raman components. The spectral width of the Rayleigh line was never resolved in this experiment (instrumental resolution ~2 cm^{-1}).

Thus the smooth collapse of the soft mode into an overdamped quasielastic component envisioned by Ginzburg is not observed, and the intense Rayleigh scattering cannot be considered as the overdamped remnant of the 207-cm^{-1} optical lattice vibration.

Brillouin scattering experiments. – In an earlier paper we discussed the room-temperature Brillouin spectrum of quartz.[9] Brillouin measurements were extended to higher temperatures in a further attempt to elucidate the origin of the critical opalescence. Spectra were recorded with phonon wave vectors in the [100], [010], [001], and [110] directions. For each propagation direction studied, the longitudinal acoustic modes exhibited a decrease in frequency of between 12 and 15% on heating from room temperature to the transition, and then an abrupt increase.

The observed temperature-dependent Brillouin shift for [100] longitudinal phonons is illustrated in Fig. 1(a) for the entire temperature range

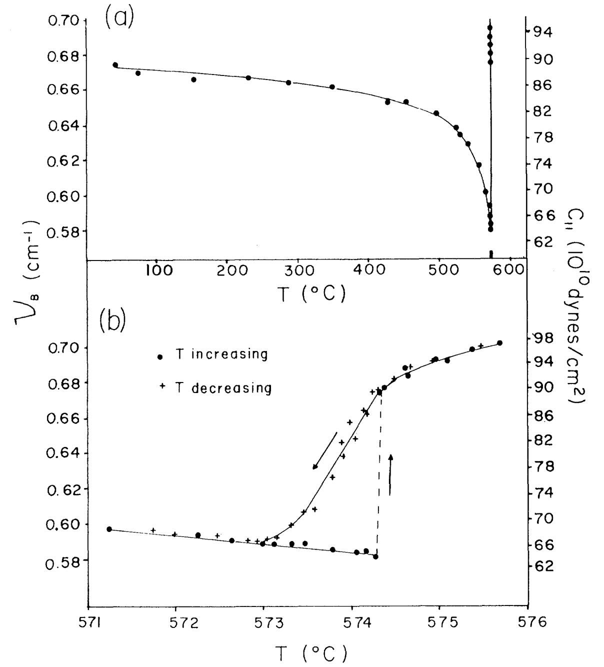

FIG. 1. The observed Brillouin shift (ν_B) and calculated elastic constant (c_{11}) versus temperature for longitudinally polarized [100] phonons. (a) 0 to 600°C. (b) Expanded temperature scale showing the critical region. The arrows indicate the direction of temperature change.

studied and in Fig. 1(b) for the critical region. On heating, the frequency exhibits an abrupt increase at 574.3°C (a sudden increase in linewidth is also observed at this point). On cooling, the frequency gradually decreases, and at 573.0 °C there is an abrupt narrowing of the Brillouin line.[10]

At these two temperatures intense Rayleigh scattering is observed. The sudden increase (to ~10^4 times the room temperature level) occurs at the same frequency as the unshifted light within the resolution of the experiment (~0.1 cm^{-1}). Here, as in the Raman experiment, there was no observed spectral structure to the opalescence. Furthermore, it should be noted that the hysteresis observed in both the Raman and Brillouin experiments implies that the transition may well be first order rather than second.

The Rayleigh linewidth.—In the Raman and Brillouin experiments the intense Rayleigh scattering in the transition region was spectroscopically indistinguishable from pure elastic scattering. Since the spectral linewidth of the "critical opalescence" was too small to measure with either the Raman spectrometer or the Brillouin interferometer, we next considered performing a light-beating experiment of the type used to measure the Rayleigh linewidth in critical opalescence in fluids.[11] This experiment was never performed since we discovered during preliminary visual observations of the scattering column that the "critical opalescence" is, in fact, elastic scattering.

When laser light is scattered from a stationary target, the scattered light exhibits a characteristic granular pattern. If the target moves slowly, the granularity also appears to move. If the target moves so rapidly that the granularity changes in a time shorter than the response time of the eye, the granularity disappears, and one sees a uniform scattered-intensity distribution. (This effect, which arises from the spatial coherence of laser light, was discussed by Rigden and Gordon in 1962.)[12]

We observed that when the crystal was below the transition temperature, the scattering column appeared to be homogeneous. [A photograph of the scattering column with 15-min exposure is shown in Fig. 2(a). The bright specks are crystal imperfections.] When the crystal was heated to the transition temperature the "fog zone" which appeared was found not to be uniform, but to exhibit the characteristic granularity associated with elastic scattering.[13] Figure 2(b) is a photograph of the scattering column in the fog zone with 2-sec exposure. The granularity is apparent in the photograph.

In Fig. 2(c) we show a photograph with 5-min exposure in the β phase. In addition to the specks caused by imperfections, there is some residual structure visible which slowly disappears as the temperature is further increased. On cooling, the above sequence is reversed, with the fog zone reappearing at a lower temperature, as we indicated earlier.

Interpretation.—The persistence of static granularity for many seconds in the light scattered from the fog zone suggests that the intense scattering is completely elastic, originating from some essentially static phenomenon rather than from thermodynamic fluctuations of the order parameter. A probable explanation of this effect was suggested by Young, who performed extensive x-ray measurements on quartz through α-β transition.[14] Young found that as the transition is approached from below, the structure separates into domains of Dauphiné (or electrical) twins. The twins, which are related by 180° rotation about the C axis, correspond to oppo-

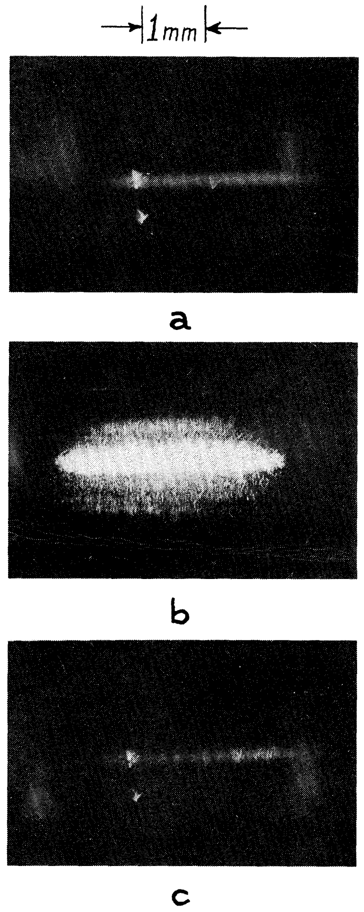

FIG. 2. Photographs of the scattering column in crystalline quartz illuminated by a 6328-Å He-Ne laser beam. (a) $T < T_c$, 15-min exposure; (b) $T = T_c$, 2-sec exposure; (c) $T > T_c$, 5-min exposure.

site signs of the order parameter η. As the transition is approached, the domain size decreases and the density of domain walls increases.

Presumably, the inhomogeneous strains present in the domain walls perturb the dielectric constant locally leading to large light-scattering efficiencies, an effect which we have previously observed in ferroelectric triglycine sulfate.[15] Thus, it is the domain walls produced by the microtwinning which we believe to be responsible for the observed opalescence. An analogous effect could occur in a fluid just below the critical point in the absence of gravity. The fluid might break up into droplets whose surfaces would produce anomalous scattering. Such an effect would occur very close to T_c since it would only become energetically possible as the surface tension vanishes.

Conclusions.– (1) Because of the static granularity of the light scattered from the fog zone, we believe that quartz does *not* exhibit critical opalescence in the usual sense of diverging fluctuations of the order parameter, despite the excellent agreement between the observed scattering intensity and the theoretical prediction based on the assumption of critical-point fluctuations. (2) The intense scattering which is observed near the transition temperature is probably a consequence of the extensive microtwinning of the Dauphiné type that occurs near the transition. (3) The hysteresis observed in the Raman and Brillouin experiments suggests that the transition is first order rather than second order. However, this distinction is not really adequate since the phenomenon of microdomain formation considerably complicates the description of the transition.

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[*] Research supported by the Advanced Research Projects Agency (Project DEFENDER) and monitored in part by the U. S. Army Research Office (Durham) and the Office of Naval Research.

[1] R. B. Sosman, *The Properties of Silica* (The Chemical Catalog Company, Inc., New York, 1927) and *The Phases of Silica* (Rutgers University Press, New Brunswick, N. J., 1965).

[2] I. A. Iakovlev, T. S. Velichkina, and L. F. Mikheeva, Dokl. Akad. Nauk SSSR 106, 675 (1956) [translation: Soviet Phys.–Doklady 1, 215 (1956)], and Kristallografiya 1, 91 (1956); I. A. Yakovlev and T. S. Velichkina, Usp. Fiz. Nauk. 63, 411 (1957) [translation: Advan. Phys. Sci. 63, 552 (1957)].

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

[4] Cf. I. L. Fabelinski, *Molecular Scattering of Light* (Plenum Press, Inc., New York, 1968).

[5] P. K. Narayanaswamy, Proc. Indian Acad. Sci. A26, 521 (1947), and A28, 417 (1948).

[6] D. A. Kleinman and W. G. Spitzer, Phys. Rev. 125, 16 (1962).

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

[8] J. F. Scott, Phys. Rev. Letters 21, 907 (1968).

[9] S. M. Shapiro, R. W. Gammon, and H. Z. Cummins, Appl. Phys. Letters 9, 157 (1966).

[10] The fog zone appears at different temperatures in the Raman and Brillouin experiments. We believe that the difference is due to a lack of temperature reproducibility after dismantling and reassembling the oven.

[11] Cf. H. L. Swinney and H. Z. Cummins, Phys. Rev. 171, 152 (1968).

[12] J. D. Rigden and E. I. Gordon, Proc. IRE 50, 2367 (1962).

[13] The first observation of this in our laboratory was by Robert W. Gammon.

[14] R. A. Young, U. S. Air Force Office of Scientific Research, Final Report No. AFOSR-2569 (unpublished), and Defense Department Documentation Center, Report No. AD 276-235, 1962 (unpublished).

[15] S. M. Shapiro, R. W. Gammon, and H. Z. Cummins, Appl. Phys. Letters 10, 113 (1967).

ACCURATE RELATIONS DETERMINING THE VOLUME DEPENDENCE OF THE QUASIHARMONIC GRÜNEISEN PARAMETER

D. John Pastine and J. W. Forbes
United States Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland
(Received 9 August 1968)

We develop a set of formulas which relate the first two volume derivatives of the temperature-independent Grüneisen parameter γ to other more readily measurable quantities. For a quasiharmonic solid in the classical temperature region, these relations are exact and permit accurate calculations of γ to second order in compression.

The temperature-independent Grüneisen parameter γ appears as the coefficient of the thermal-pressure term of a quasiharmonic (qh) solid in the classical region of temperature T. For such a solid the relationship between pressure P, specific volume V, and temperature T is given exactly by[1]

$$P=P_0(x)+\rho_i(\gamma/x)E_T(x,T), \tag{1}$$

where $x=V/V_i$, V_i is the specific volume under normal conditions, $E_T(x,T)$ is the thermal energy, $\rho_i=1/V_i$, and $P_0(x)$ is a function of volume only. The total energy $E(x,T)$ is given by[1]

$$E(x,T)=E_0(x)+E_T(x,T), \tag{2}$$

where $E_0(x)$ is a function only of volume. With (1) and (2) it follows immediately that

$$\gamma(x)=\frac{x}{\rho_i}\left(\frac{\partial P}{\partial E}\right)_x=V\left(\frac{\partial P}{\partial E}\right)_V. \tag{3}$$

Since in this (the qh) approximation γ is independent of T and is therefore a function of volume only, its values can be ascertained if the derivative $(\partial P/\partial E)_x$ can be evaluated along any path for which the relationship between P, E, and x is given. At present this is most easily done at individual points along the Hugoniot.[2] For materials of low yield point which are initially at normal pressure and then subjected to shock compression, the hydrostatic shock pressure P_h is given by[2]

$$P_h=\rho_iU_su_p, \tag{4}$$

where U_s is the shock velocity and u_p is the velocity of matter behind the shock front. Likewise the energy E_h behind the shock front is given by[2]

$$E_h=E_i+P_h\frac{(u_p/U_s)}{(2\rho_i)}, \tag{5}$$

where E_i is the initial value of specific energy. The relative compression x is given by[2]

$$x=1-u_p/U_s, \tag{6}$$

The relationship between U_s and u_p is given by an expression of the form[3]

$$U_s=C_i+b_1u_p+b_2u_p^2+\cdots, \tag{7}$$

where C_i is the bulk sound speed (i.e., $C_i^2=B_s/\rho_i$, where B_s is the isentropic bulk modulus) in the normal state and b_1 and b_2 are functions only of the initial conditions.[3] Since in this development the initial pressure is always (effectively) zero, the quantities E_i, C_i, ρ_i, b_1, and b_2 may be viewed as functions only of the temperature T_i along the zero-pressure isobar. With the relations (4) through (7) it is possible to find analytic expressions for P_h as a function of x and E_h as a function of x which depend only on the initial temperature T_i. For example, if U_s is approximated by only the first two terms in the expansion (7), one can derive the expressions

$$P_h=\rho_iC_i^2(1-V/V_i)[1-b_1(1-V/V_i)]^{-2}, \tag{8}$$

$$E_h=E_i+\frac{P_h(1-V/V_i)}{2\rho_i}. \tag{9}$$

To evaluate γ in this approximation it is only necessary to calculate the variation of P_h and E_h with the initial conditions (i.e., the initial tem-

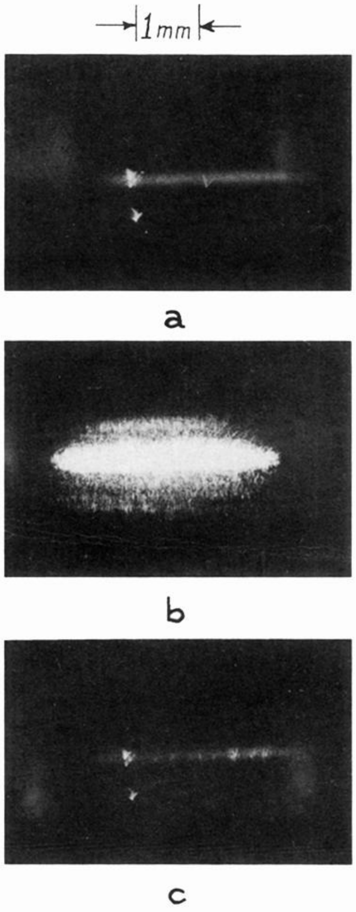

FIG. 2. Photographs of the scattering column in crystalline quartz illuminated by a 6328-Å He-Ne laser beam. (a) $T < T_c$, 15-min exposure; (b) $T = T_c$, 2-sec exposure; (c) $T > T_c$, 5-min exposure.