Comment on the Elastic Constants of Alpha-Quartz

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Atanasoff and Hart[1] have recently described some admirable experiments on the vibrations of variously oriented crystal quartz plates. Their results, however, for the elastic constants of quartz, calculated on the assumption that the plates were infinite, evince a small but unexplained discrepancy with the classical elastic theory for substances possessing the symmetry of quartz, namely crystal class D_3.

Now Cady[2] has shown that in the calculation of the eigenfrequencies of a piezoelectric crystal, the forces arising from the polarization produced by the vibration must be taken into consideration. This has not been done by Atanasoff and Hart, and the object of this letter is to show that when cognizance is taken of the converse piezoelectric effect, the discrepancy between elastic theory and experiment is removed.

If, in an anisotropic substance, u is the displacement vector, θ the strain tensor, φ the stress tensor, c the elastic tensor, F the volume rate of force developed by the stress tensor, E the electric field intensity, P the polarization, and e the piezoelectric tensor, we have:

$$\theta_{ij}=\tfrac{1}{2}\left(\frac{\partial u_i}{\partial x_i}+\frac{\partial u_j}{\partial x_i}\right), \tag{1}$$

$$\varphi_{ij}=\sum_{\alpha\beta} c_{ij\alpha\beta}\theta_{\alpha\beta}-\sum_{\gamma} e_{ij\gamma}E_\gamma, \tag{2}$$

$$F_j=\frac{\partial\varphi_{ij}}{\partial x_i}=\rho\ddot{u}_j=\sum_{\alpha\beta} c_{ij\alpha\beta}\frac{\partial^2 u_\alpha}{\partial x_i\partial x_\beta}-\sum_{\gamma} e_{ij\gamma}\frac{\partial E_\gamma}{\partial x_i}, \tag{3}$$

$$P_i=\sum_{\alpha\beta} e_{\alpha\beta i}\theta_{\alpha\beta}+k_iE_i, \tag{4}$$

where k_i is a principal electric susceptibility. Now by symmetry, for an infinite plate oriented perpendicular to the x_i direction, we have:

$$\theta_{\alpha\beta}=\theta_{\alpha\beta}\delta_{\beta i}, \tag{5}$$

$$\frac{\partial E_\gamma}{\partial x_j}=\frac{\partial E_\gamma}{\partial x_j}\delta_{ij}. \tag{6}$$

If cognizance is taken of Eqs. (5) and (6), the second of Maxwell's equations yields:

$$4\pi e_{\alpha ii}\frac{\partial\theta_{\alpha i}}{\partial x_i}=-K_i\frac{\partial E_i}{\partial x_i}, \tag{7}$$

where K_i is a principal dielectric constant.

The first and third of Maxwell's equations yield, to within the precision of the calculation:

$$\partial^2E_\gamma/\partial x_i^2=0 \quad \text{for} \quad \gamma\neq i. \tag{8}$$

The foregoing relation is a consequence of the fact that the wave-length of the resulting electric wave is very long compared with the wave-length of the elastic wave.

We now assume that the external field is zero. The differential equations (3), (7) and (8) must be solved subject to the boundary conditions:

$$\sum_\alpha \theta_{\alpha i}c_{ij\alpha i}-\sum_\gamma e_{ij\gamma}E_\gamma=0,$$
$$K_\gamma E_\gamma+\sum_\alpha e_{\alpha i\gamma}\theta_{\alpha\gamma}=0. \tag{9}$$

This requires that $E_\gamma=0$ for $i\neq\gamma$. Our differential equation for the propagation of elastic waves then becomes:

$$\rho\ddot{u}_j=\sum_\alpha\left\{c_{ij\alpha i}+\frac{4\pi e_{iji}e_{\alpha ii}}{K_i}\right\}\frac{\partial^2 u_\alpha}{\partial x_i^2}. \tag{10}$$

If we assume

$$u_j=A_j\cos\frac{n\pi x_i}{s}e^{i\omega t}$$

the condition that Eq. (10) be satisfied is the secular system:

$$\sum_\alpha c^*_{ij\alpha i}A_\alpha-\kappa^2A_j=0, \tag{11}$$

where

$$c^*_{ij\alpha i}=c_{ij\alpha i}+\frac{4\pi e_{iji}e_{\alpha ii}}{K_i}$$

and

$$\kappa^2=4\rho s^2f^2/n^2, \quad f=\omega/2\pi, \tag{12}$$

where s is the thickness of the plate and f is the observed resonant frequency.

The use of Atanasoff and Hart's data for the resonant frequencies of vibration of variously oriented plates, and the assumption that quartz is trigonal yields the elastic constants of quartz and several internal checks. These constants are shown in Table I and compared with those computed from Atanasoff and Hart's incomplete theory and those observed statically by Voigt.[3]

The internal consistency of the data verifies that quartz is trigonal. This may best be shown by calculating some resonant frequencies and comparing these with observed frequencies not used in the calculation of the elastic constants. Thus for a (30°, −38°12½′) plate:

$$\kappa^2 \text{ calc.}=64.86\times10^{10} \text{ dynes/cm}^2,$$
$$\kappa^2 \text{ obs.}=64.92\times10^{10} \text{ dynes/cm}^2,$$

and for a (30°, 0°) plate:

$$\kappa^2 \text{ calc.}=49.36\times10^{10} \text{ dynes/cm}^2,$$
$$\kappa^2 \text{ obs.}=49.39\times10^{10} \text{ dynes/cm}^2.$$

The differences between the observed and computed values are within the experimental errors of the quantities involved.

The value used for e_{11} was 5.29×10^4 e.s.u. units as reported by Van Dyke,[4] and the values for K_i were taken directly from Cady's paper.

One other point should be noted. Atanasoff and Hart used an air gap between the crystals and the plates

Table I. *Elastic constants of alpha-quartz. The units are 10^{10} dynes/cm².*

	Voigt	Atanasoff and Hart Uncorrected	Atanasoff and Hart Corrected
c_{11}	86.8	87.55	86.75
c_{12}	7.1	6.07	6.87
c_{44}	58.2	57.19	57.86
c_{14}	17.2	17.25	17.96
c_{13}	14.4	13.3	11.3
c_{33}	107.5	106.8	106.8

exciting the vibrations. Thus the external field is not zero, and this produces another shift in the fundamental frequency, of the same order of magnitude but opposite to that contemplated here. However, Cady has shown that this correction decreases as $1/n^2$ and since n is very large in the experiments under review, this correction is negligible.

[1] J. V. Atanasoff and P. J. Hart, Phys. Rev. **59**, 85 (1941).
[2] W. G. Cady, Physics **7**, 237 (1936).
[3] W. Voigt, *Lehrbuch der Kristallphysik* (Teubner, Leipzig, 1928).
[4] K. S. Van Dyke, Phys. Rev. **42**, 587 (1932).

Note on the Structure of Liquid Helium

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1. The existence of surface transfer films of liquid helium II of the order of 100 atoms in thickness[1] has sometimes seemed difficult to understand, although actually this thickness is in accord with the usual theory of interatomic forces. The difference between the $1/r^6$ van der Waals interactions of two helium atoms and of a helium atom and an atom of the solid container yields a $1/a^3$ dependence on the distance from the surface. In the case of a metallic container, there is also a comparable $1/a^3$ energy arising from interaction with the electrons of the metal.[2] If a solid surface projects out of a reservoir of liquid helium II, the thickness a_h of the film at a height h cm above the free surface of the liquid is obtained by equating the total interaction energy to the gravitational potential energy of a helium atom. This gives for copper: $a_h=4.3\times 10^{-6}/h^{\frac{1}{3}}$ cm, which is in excellent agreement with the rather uncertain experimental value of 3.5×10^{-6} cm for a sheet extending a few cm above the liquid surface.[1] The numerical value 4.3 for copper is replaced by 4.7 for silver, ~4 for glass, and 2.2 for rocksalt (100 plane exposed). Although such films probably exist in general, this simple calculation is valid only when the fluid under consideration is sufficiently nonviscous so that it can come into equilibrium under these forces before it evaporates; this explains the failure to observe such films with helium I.[1] Accurate measurements of film thickness would give useful information about long range interatomic forces.

2. The phase transition in liquid helium appears to be a continuous one in the sense that all properties of the state that do not involve differentiation with respect to the temperature are continuous.[3] It is therefore plausible to assume that helium I consists of a single phase A and helium II of a mixture of two phases A and B, phase B being absent at the λ-point and growing continuously at the expense of phase A as the temperature decreases. This point of view was proposed by Tisza[4] and developed by H. London;[5] they showed that the experiments could be understood, qualitatively at least, by assuming that A is disordered and has a normal viscosity, while B is ordered and has little or no viscosity. However, there appears to be no need to assume, as has sometimes been done,[5,6] that the liquid in the surface layer is qualitatively different from that in the volume of the fluid, since the capillary experiments can be understood equally well in terms of the viscous drag exerted by a nearby wall on phase A. Moreover, a different structure of the surface layer could be expected only if the interaction of an atom with the wall were comparable with the interaction with its neighbors. The calculations of paragraph 1 indicate that this is true only for the first 2 or 3 atom layers, while the thermomechanical effect is appreciable for much larger channels.[7]

3. The phase A referred to in paragraph 2 can be understood in terms of an Einstein-Bose gas model, in which each helium atom moves in the periodic field that approximately represents the effect of correlations between the positions of the atoms. This model explains the x-ray data, the position of the λ-point[8] and the positive temperature coefficient of viscosity of helium I.[3,4] Its application to phase B does not, however, explain the observed specific heat anomaly,[9] and the failure of a more complete treatment[10] to accomplish this makes it seem likely that no gas model will succeed here. It is natural then to assume a more typically liquid model for phase B, in which there exists a discrete energy level for each atom. Because of the weak attractive forces and large zero-point kinetic energy of helium atoms there will not be more than one such state per atom, if any, and it would probably lie $\sim 10^{-4}$ ev below the continuum of phase A states. These "bound" atoms would diffract over several atom distances, so that the aggregation would not possess the rigidity of a lattice. The energy of a given bound atom could depend on the number of its neighbors that are similarly bound; the inclusion of an "ordering energy" of this type would favor the transition from A to B and sharpen the specific heat curve. Further, volume-conserving deformations would not alter the energy of phase B, and the adiabatic nature of laboratory manipulations as compared with the period of the system ($\sim 10^{-10}$ sec. for B states depressed by 10^{-4} ev) would make excitation to continuum states extremely improbable. There would thus be no resistance to deformation, no mechanism for dissipating flow energy, and hence no viscosity. While this model has some physical plausibility to recommend it, it must be regarded as tentative because of the great difficulty of calculating the several parameters that appear in it in terms of atomic properties.

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[1] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. **A170**, 429 (1939).
[2] J. Bardeen, Phys. Rev. **58**, 727 (1940).
[3] W. H. Keesom and G. E. MacWood, Physica **5**, 737 (1938), have obtained data that indicate a possible discontinuity in the viscosity at the λ-point. The improbability of the coexistence of distinct thermodynamic states having the same energy and free energy makes a further experimental investigation of this point desirable.
[4] L. Tisza, Nature **141**, 913 (1938).
[5] H. London, Proc. Roy. Soc. **A171**, 484 (1939).
[6] F. London, Phys. Rev. **54**, 947 (1938).
[7] J. F. Allen and H. Jones, Nature **141**, 243 (1938); J. F. Allen and J. Reekie, Nature **144**, 475 (1939).
[8] Cf. reference 6. From the present point of view the λ-temperature depends essentially on the properties of phase A, and may be changed somewhat by introducing an effective mass for the helium atoms due to their motion in the periodic field (cp. electronic effective mass in the theory of metals).
[9] W. H. Keesom and A. P. Keesom, Physica **2**, 557 (1935).
[10] L. I. Schiff, Phys. Rev. **59**, 758 (1941).