Internal Strain and Raman-Active Vibrations in Solids

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In lattices in which not all ions possess inversion symmetry, internal-strain effects give rise to piezoelectricity and contribute to the elastic response. It is possible to describe these internal strains as static optical-phonon-mode displacements and to analyze the internal-strain contributions to the elastic and piezoelectric constants accordingly. Certain symmetry properties become evident as a result, the most general of which is that only Raman-active modes contribute to internal strain, and only modes simultaneously Raman- and infrared-active produce piezoelectricity. This formalism also provides a basis for a discussion of piezoelectric and elastic anomalies which may accompany incipient instabilities in optical-phonon modes. Finally, it is shown that the anomalous elastic behavior of β quartz near the α-β transition temperature can be understood by postulating a low-frequency temperature-dependent Raman-active mode of A_1 symmetry.

INTERNAL-strain effects in a solid lead to contributions to the elastic and piezoelectric constants,[1] which have been studied from the viewpoint of lattice dynamics by several authors, including Born and Huang and Cochran.[2] In particular, Cochran has discussed how a soft optical mode leads to elastic and piezoelectric anomalies via internal-strain effects. In this paper we further develop the discussion of these properties by the introduction of a second-rank tensor[1] which plays a fundamental role in the internal-strain contribution to the elastic and piezoelectric constants, in the relation of elastic and optical properties, and in the derivation of symmetry relations. The general symmetry relations can be summarized as follows: Only Raman-active modes contribute to the internal-strain part of the elastic constants and only modes which are both Raman and infrared active contribute to the piezoelectric coefficients. The elastic anomalies near the α-β phase transition of quartz are discussed as an application of the general results, and it is shown that the hypothesis of a soft Raman-active mode of A_1 symmetry leads to good agreement with the observed elastic behavior of β quartz.

Let us consider the properties of a long-wavelength acoustic lattice vibration, using the rigid-ion model. The ionic displacements for an acoustic vibration of wave vector $\mathbf{p}$ and branch j_a are

$$u_\alpha(l,k)=m_k^{-1/2}w_{\alpha k}(j_a,\mathbf{p})\exp[i\mathbf{p}\cdot\mathbf{x}(_k^l)-i\omega(j_a,\mathbf{p})t], \quad (1)$$

where $\mathbf{w}_k$ denotes the reduced displacement of sublattice k. (The notation will generally follow that of Born and Huang,[1] except where other symbols are explicitly defined.) The perturbation method of solution of the equations of motion for the ionic displacements due to Born and Huang[1] is a power-series expansion of all quantities in terms of the magnitude ϵ of the wave vector $\mathbf{p}$ along a fixed direction of propagation denoted by the unit vector $\hat{p}$. Thus the power series for the reduced displacement is

$$w_{\alpha k}(j_a,\epsilon\hat{p})=w_{\alpha k}{}^{(0)}(j_a,\hat{p})+i\epsilon w_{\alpha k}{}^{(1)}(j_a,\hat{p})+\tfrac{1}{2}\epsilon^2 w_{\alpha k}{}^{(2)}(j_a,\hat{p})+\cdots, \quad (2)$$

and similar expansions apply to the frequency $\omega(j_a,\epsilon\hat{p})$ and dynamical matrix $\bar{\mathbf{C}}(\epsilon\hat{p};kk')$. The substitution of the expansions into the equation of motion yields a separate equation for each order of ϵ.

The solution of the zero-order equation in ϵ is $w_{\alpha k}{}^{(0)}(j_a,\hat{p})=m_k^{1/2}v_\alpha(j_a,\hat{p})$ and $\omega^{(0)}=0$, where $\mathbf{v}(j_a,\hat{p})$ is an arbitrary vector. To express the solutions of the first- and second-order equations in terms of a second-rank tensor we introduce the eigenvectors $e_{\beta k}(j)$ and eigenvalues $\omega_e^2(j)$ of the dynamical matrix at $p=0$ by

$$\bar{C}_{\alpha\beta}{}^{(0)}(kk')e_{\beta k'}(j)=\omega_e^2(j)e_{\alpha k}(j) \quad (3)$$

and the notation $\bar{C}_{\alpha\beta;\,\gamma_1\cdots\gamma_n}{}^{(n)}$ will indicate the derivative of order n of the dynamical matrix with respect to $p_{\gamma_1}\cdots p_{\gamma_n}$; we adopt the convention of summing over repeated indices. Then if we expand the internal strain $w^{(1)}$ in terms of the complete set of eigenvectors $\mathbf{e}(j)$ as

$$w_{\alpha k}{}^{(1)}(j_a,\hat{p})=\sum_j q_j(j_a,\hat{p})e_{\alpha k}(j), \quad (4)$$

we find from the first-order equation that the coefficients are given by

$$q_j(j_a,\hat{p})=-\frac{F_{\beta\gamma}(j)}{\omega_e^2(j)}v_\beta(j_a,\hat{p})\hat{p}_\gamma+Z_k m_k^{-1/2}\frac{e_{\alpha k}(j)}{\omega_e^2(j)}E_\alpha, \quad (5)$$

where $\mathbf{E}$ is the macroscopic electric field, Z_k is an effective charge, and the second-rank tensor of optical mode j is defined as

$$F_{\beta\gamma}(j)=[\bar{C}_{\alpha\beta;\,\gamma}{}^{(1)}(kk')m_{k'}{}^{1/2}]e_{\alpha k}(j). \quad (6)$$

The expansion coefficient q_j for an acoustic mode j may be chosen to vanish. By using the expansion of the internal strain in optical-mode eigenvectors [Eqs. (4)–(5)] the solubility condition for the second-order equation leads to an internal-strain contribution $(\alpha\gamma,\mu\delta)$

[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1962), Chap. V.
[2] W. Cochran, Advan. Phys. **10**, 401 (1961).

to the elastic constant $c_{\alpha\gamma,\mu\delta}$ given by

$$(\alpha\gamma,\mu\delta)=-\sum_j \frac{1}{\omega_e^2(j)}F_{\alpha\gamma}(j)F_{\mu\delta}(j) \qquad (7)$$

and to a piezoelectric coefficient $e_{\mu,\alpha\gamma}$ given by

$$e_{\mu,\alpha\gamma}=-\sum_j \frac{1}{\omega_e^2(j)}F_{\alpha\gamma}(j)P_\mu(j), \qquad (8)$$

where $\mathbf{P}(j)$ is the polarization of mode j, $P_\mu(j)=\sum_k Z_k m_k^{-1/2}e_{\mu k}(j)$. The advantages of introducing the second-rank tensor $F_{\alpha\beta}$ become apparent in the subsequent discussion of symmetry properties and elastic anomalies.

From the defining equation for $F_{\alpha\beta}(j)$, one sees that since $\sum_{k'}\bar{C}_{\alpha\beta;\,\gamma}{}^{(1)}(kk')m_{k'}{}^{1/2}$ is a characteristic third-rank tensor of the crystal, then $F_{\alpha\beta}(j)$ transforms as the eigenvector $\mathbf{e}(j)$ under the point-group operations. Since $F_{\alpha\beta}(j)$ also transforms as a second-rank tensor, it follows that only eigenvectors which transform as second-rank tensors contribute to $F_{\alpha\beta}(j)$. The eigenvectors which transform as second-rank tensors are Raman active[3]; hence we see from Eqs. (7) and (8) that only Raman-active modes contribute to $\mathbf{F}$ and thus to the internal-strain part of the elastic constants and only modes which are both Raman and infrared active contribute to the peizoelectric coefficients. Additional symmetry requirements are imposed upon the tensor $F_{\alpha\beta}(j)$ by the condition that the tensor components $e_{\mu,\alpha\gamma}$ and $(\alpha\gamma,\mu\delta)$ must also form bases for an identity representation of the crystal space group. We note that the frequency and polarization of the optical modes at $\mathbf{p}=0$ which appear in $(\alpha\gamma,\mu\delta)$ and $e_{\mu,\alpha\gamma}$ are directly measurable in Raman effect and infrared reflectivity experiments.

The preceding discussion has been based on the rigid-ion model. A more general study of the elastic properties of crystals with polarizable atoms has been carried out by Cowley,[4] who bases his discussion on the shell model. His result for each of the brackets $(\alpha\gamma,\mu\delta)$ and $e_{\mu,\alpha\gamma}$ is a sum of a lattice term (arising from the core displacement) plus an electronic term (from the shell displacement). By introducing the eigenvectors and eigenvalues of the dynamical matrix at $\mathbf{p}=0$ one may then express his result for the lattice part in terms of a second-rank tensor in the same form as given in the rigid-ion model by Eqs. (7)–(8). Thus in a polarizable atom model our previous comments will apply to the lattice part of the brackets $(\alpha\gamma,\mu\delta)$ and $e_{\mu,\alpha\gamma}$.

It is well established that certain ferroelectric instabilities develop as a result of long-wavelength $(\mathbf{p}\to 0)$ polar phonons whose frequencies are both anomalously low and strongly temperature-dependent.[5]

[3] See, for example, R. Loudon, Advan. Phys. **13**, 423 (1964).
[4] R. A. Cowley, Proc. Roy. Soc. (London) **A268**, 121 (1962).
[5] W. Cochran, Advan. Phys. **9**, 387 (1960); A. S. Barker and M. Tinkham, Phys. Rev. **125**, 1527 (1962); R. A. Cowley, *ibid.* **134**, A981 (1964).

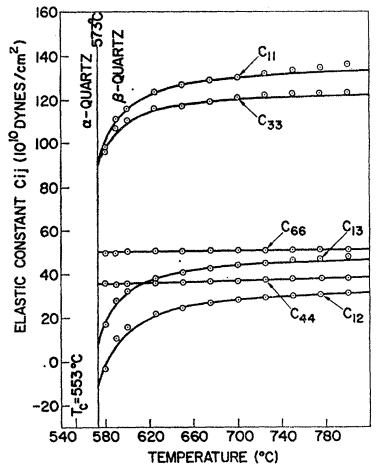

FIG. 1. The temperature dependence of the elastic constants of β quartz. Open circles are measured values (Ref. 6). C_{44} and C_{66} exhibit a slight linear temperature dependence. ($C_{66}=\frac{1}{2}[C_{11}-C_{12}]$ is not independent but is shown for convenience.) The remaining elastic constants are fitted to Eq. (9) with $T_c=553$°C and the following values for $C^0(ij)$ (in units of 10^{10} dyn/cm^2): (11)=137, (12)=35.5, (33)=125, (13)=50. The $\Delta C(ij)$ (in units of 10^{10} dyn °C/cm^2) are: (11)=(12)=990, (33)=719, (13)=[(11)(33)]$^{1/2}$=844.

The additional advantage of the reformulated equations (7) and (8) is the explicit appearance of the phonon frequencies $\omega_e(j)$, making it immediately obvious that an anomalously "soft" polar mode that is also Raman active (which is possible in all of the 20 piezoelectric crystal classes) will necessarily affect not only the dielectric response, but the elastic and piezoelectric properties as well. Cochran has discussed the hypothetical behavior of a ferroelectric zinc-blende lattice extensively from this point of view.[2] It is not, however, necessary to restrict our attention exclusively to polar modes. We can imagine a lattice becoming unstable toward a non-polar-optic mode as well, and Eq. (7) shows that if the "soft" mode is Raman active, large anomalous internal-strain contributions to one or more elastic constants must result. In fact we can establish the following rather surprising result: It is not possible for a Raman-active mode frequency $\omega_e(j)$ to go to zero (as in a second-order transition) without first precipitating an instability of a different sort, i.e., with respect to a homogeneous elastic deformation. [At least one elastic constant of the form C_{ii} will become negative before $\omega_e(j)\to 0$, violating a necessary condition for stability against homogeneous deformations.]

At about 573°C, ordinary low-temperature α quartz undergoes a reversible phase transformation into a more symmetric β-quartz structure. Among the several anomalies clearly associated with this transition, the pronounced temperature dependence of the elastic constants in the immediate vicinity of the transition temperature, as shown in Fig. 1, is perhaps the most striking.[6] β quartz belongs to the space group $D_6{}^4(P6_222)$

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

and the number of $\mathbf{p}=0$ optical-normal modes transforming according to the various irreducible representations of the factor group D_6 are as follows: $A_1(1)$, $B_1(3)$, $A_2(3)$, $B_2(2)$, $E_1(5)$, and $E_2(4)$. In connection with internal strain, only the Raman-active modes A_1, E_1, and E_2 need be considered. The requirement that $\mathbf{F}(A_1)$ transform irreducibly restricts the nonvanishing components to $F_{xx}(A_1)=F_{yy}(A_1)$ and $F_{zz}(A_1)$. Similarly E_1 modes contribute components of the form $F_{xz}(E_1)$ and $F_{yz}(E_1)$, and E_2 modes contribute $F_{xx}(E_2)=-F_{yy}(E_2)$ and $F_{xy}(E_2)$. A consideration of the over-all symmetry requirements on the elastic constants $(xz,xz)=(yz,yz)$ and $2(xy,xy)=(xx,xx)-(xx,yy)$ imposes the further restrictions $|F_{xz}(E_1)|=|F_{yz}(E_1)|$ and $|F_{xx}(E_2)|=|F_{xy}(E_2)|$. Inspection of Eq. (7) shows that the A_1 mode makes internal-strain contributions to the elastic constants C_{11}, C_{12}, C_{13}, and C_{33}, but not to C_{44} or C_{66}, whereas E_1 modes contribute only to C_{44} and E_2 modes contribute to C_{11}, C_{12}, and C_{66}. It is clear with reference to Fig. 1 that a large internal-strain contribution brought about by a low-frequency A_1 mode provides an attractive possible explanation for the behavior of the elastic constants of quartz.

We have investigated this idea more quantitatively by assuming the A_1 phonon mode in question has a renormalized frequency whose temperature dependence[4] is of the normal high-temperature form $\omega^2(A_1)=\omega_0^2+\alpha T$. This in turn leads to the following form for the anomalous elastic constants:

$$C_{ij}=C_{ij}^0-\Delta C_{ij}/(T-T_c), \tag{9}$$

where C_{ij}^0 is the (approximately) temperature-independent contributions from both non-internal-strain terms and internal-strain terms associated with higher-frequency modes (which are, therefore, relatively less temperature-dependent). Simple relations among the ΔC_{ij} in addition to those imposed by the over-all symmetry of the elastic constants nearly always result if modes of a single symmetry type contribute predominantly to the internal strain, as is certainly the case for the type of anomaly under discussion. Such relations should be valuable in establishing whether or not an experimentally observed elastic anomaly involves large internal-strain contributions. For β quartz the form of $F(A_1)$ dictates that $\Delta C_{11}=F_{xx}(A_1)^2/\alpha=\Delta C_{12}$ and $[\Delta C_{13}]^2=[F_{xx}(A_1)F_{zz}(A_1)/\alpha]^2=\Delta C_{11}\Delta C_{33}$. That expressions of this form do indeed provide a reasonable representation of the β-quartz elastic data is shown in Fig. 1, where the calculated curves satisfy these relations.

Two points deserve some additional comment. First of all, the current interpretation of Raman-scattering results on β quartz[7] places the single A_1 mode at $\sim$452 cm^{-1} with no exceptional temperature dependence implied, which seems inconsistent with the present formulation. (More recent Raman-scattering experiments,[8] while offering no confirmation of our conjecture, seem, however, to leave the published interpretation somewhat in doubt.) Also, Kleinman and Spitzer[9] find a remarkably strong similarity between the spontaneous atomic displacements involved in the α-β quartz transition and a calculated vibrational eigenvector of α quartz. However, neither this calculated eigenvector nor the spontaneous displacements bear any direct relation to the A_1 eigenvector of β quartz and in fact they transform very nearly according to the B_1 representation of the β quartz factor group. Thus while the present proposal does reasonably account for the elastic anomalies of β quartz, it represents at best only the beginnings of a comprehensive dynamical description of the α-β phase transition.

[7] P. K. Narayanaswamy, Proc. Indian Acad. Sci. **28**, 417 (1948).
[8] S. M. Shapiro, D. C. O'Shea, and H. Z. Cummins, Phys. Rev. Letters **19**, 361 (1967).
[9] D. A. Kleinman and W. G. Spitzer, Phys. Rev. **125**, 16 (1962).

Erratum

Lattice Absorption in Finite Crystals, MARVIN HASS AND HERBERT B. ROSENSTOCK [Phys. Rev. **153**, 962 1967)]. Equation (2.8a) should be

$$u_n(2j-1)=c_b[\sin(2j-1)k_na-(1-M_2\omega_n^2/\beta)\sin(2j-2)k_na].$$

Equation (2.8b) should be

$$u_n(2j)=c_b[-\sin(2j-1)k_na+(1-M_1\omega_n^2/\beta)\sin 2jk_na].$$