$\times 10^{-8}$ eV cm, $\Delta = 1.0$ eV, and for the remaining parameters, the values identical to HgSe. The quantities A', M, L', and $(L-M-N)$ are given in units of $\hbar^2/2m_0$.

As can be seen in Figs. 1 and 2, the effective-mass change with E_g at $\sim 10^{17}$ cm^{-3} is very similar to the prediction from the three-band approximation. However, for the concentration $\sim 5\times 10^{18}$ cm^{-3} in HgSe and $\sim 2\times 10^{19}$ cm^{-3} in HgTe the behavior is qualitatively different. The strongest deviation takes place at $E_g = 0$. Values of pressure P given in the figures were calculated assuming that $dE_g/dP = 1.4\times 10^{-5}$ eV/atm, and that $E_g(P=1 \text{ atm}, T=4.2°\text{K}) = 0.22$ eV for HgSe and $E_g(P=1 \text{ atm}, T=4.2°\text{K}) = 0.03$ eV for HgTe.

We also consider the influence of different values of Δ on the behavior. As indicated in Fig. 2, a decrease in Δ accentuates the increase in m^* with pressure at high donor concentrations. Thus, the increase in m^* with pressure may occur at lower donor concentrations than expected for Δ constant, if Δ is decreasing with pressure.

We have shown that higher band interactions must be considered for the effective-mass determination in narrow-gap semiconductors with high carrier concentrations. These results should be particularly important in the evaluation of pressure and temperature dependence of m^* in semimetals and narrow-gap semiconductors.

---

†Work supported in part by the U. S. Army Research Office (Durham) and by the Advanced Research Projects Agency.

*On leave from the Institute of Physics, Polish Academy of Sciences, Warsaw, Poland.

[1]S. Groves and W. Paul, Phys. Rev. Lett. 11, 194 (1963).

[2]R. Piotrzkowski, S. Porowski, Z. Dziuba, J. Ginter, W. Giriat, and L. Sosnowski, Phys. Status Solidi 8, K135 (1965).

[3]R. Piotrzkowski and S. Porowski, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, R. I., 1967*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 1090.

[4]E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).

[5]R. R. Galazka, D. G. Seiler, and W. M. Becker, in Proceedings of the Conference on Semimetals and Narrow Gap Semiconductors, American Physical Society Topical Meeting, Dallas, Tex., 20 March 1970 (to be published).

[6]J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, England, 1960).

[7]D. G. Seiler, R. R. Galazka, and W. M. Becker, to be published.

[8]C. R. Pidgeon and S. H. Groves, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, R. I., 1967*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 1080.

RAMAN STUDIES OF UNDERDAMPED SOFT MODES IN $PbTiO_3$ *

Gerald Burns and B. A. Scott
IBM Watson Research Center, Yorktown Heights, New York 10598

(Received 24 February 1970)

Unlike other ferroelectric perovskites, $PbTiO_3$ displays temperature-dependent Raman spectra consisting of underdamped modes, including the "soft" transverse-optical (TO) modes. Moreover, the softest TO mode shows linewidth divergence at the ferroelectric-to-paraelectric transition. Also in contrast to previously studied perovskites, Raman selection rules are rigorously obeyed in both the ferroelectric and paraelectric states.

In this Letter we report the temperature dependence of the Raman spectra of the perovskite ferroelectric[1] $PbTiO_3$. Our results differ substantially from those reported for related perovskite ferroelectrics[2-5] in the following respects. (a) All modes in $PbTiO_3$, including the "soft" transverse-optic (TO) modes, are underdamped in the ferroelectric state up to the transition temperature $T_c \cong 493$°C. At T_c, the ratio of damping coefficient to lowest transverse-mode frequency, γ/ω_0, approaches 0.5 ($>\sqrt{2}$ is overdamped). Thus, the mode no longer has a simple shape from which ω_0 can be obtained from the peak position and γ from the full linewidth at half-maximum intensity. Rather, the line was fitted using a classical damped-oscillator model to obtain γ and ω_0, with excellent agreement between experimental and calculated line shapes. (b) For the first time, a damping constant has been observed which diverges as T_c is approached.[6] (c) The Raman selection rules in the C_{4v} ferroelectric state are rigorously obeyed. (d) Since the modes are theoretically inactive in the cubic (O_h) paraelectric phase, and the transition at T_c is first order, the modes abruptly disappear on heating through the transition temperature.

Crystals of $PbTiO_3$ used in this study were grown from PbO-TiO_2-B_2O_3 melts using the phase-equilibrium data of Sholokhovich.[7] Raman measurements were obtained with a 70-mW He-Ne laser at 6328 Å and a Jarrell-Ash double monochromator.

Figure 1 depicts typical spectra. As can be seen, the lines are sharp and appear only in the appropriate polarization. Only the $x(zz)y$ spectrum,[8] which allows TO modes of A_1 symmetry, shows a strong extraneous line at ~150 cm^{-1}. The totally symmetric A_1 spectrum is commonly observed to contain extraneous lines. Also shown in the insert in Fig. 1 is the lowest E(TO) mode at two temperatures near T_c. Here it is clear that the mode is underdamped, although the linewidth is about half the peak position. To obtain the damping coefficient γ and position ω_0 from such lines the usual damped classical harmonic-oscillator equations were used. The dielectric constant is given by

$$\epsilon(\omega)-\epsilon_\infty=\frac{S\omega_0^2}{\omega_0^2-\omega^2+i\omega\gamma}. \tag{1}$$

Since Raman emission is proportional to the imaginary part of the dielectric constant, $\epsilon''(\omega)$, the Raman line intensity is given by[4]

$$I_r(\omega)\propto\frac{kTP_s^2\epsilon'(0)\gamma\omega_0^2}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}, \tag{2}$$

where P_s is the spontaneous polarization and $\epsilon'(\omega)$ is the real part of the dielectric constant. For $\gamma/\omega_0 \ll 1$, γ is simply the full width at half-maximum intensity. When $\gamma/\omega_0 \sim 1$, Eq. (2) must be used to calculate the line as shown in Fig. 1 (insert). As can be seen, excellent fits have been obtained.

Figure 2 shows γ as a function of temperature. Here, γ appears to have a singularity slightly above T_c. A singular behavior for the damping constant has been predicted theoretically based on a one-dimensional model.[9] However, for a three-dimensional model the same interaction no longer yields singular behavior for γ.[10] Note that γ applies to the "soft" transverse E mode, the frequency of which is related by the Lyddane-Sachs-Teller (LST) relationship to ϵ_x, the dielectric constant perpendicular to the ferroelectric axis. Nevertheless, from the similarity between $\gamma(T)$ and the known temperature divergence of ϵ_z, the following approach was successfully employed. From the Devonshire free-energy expansion in terms of even powers of the polarization P, where A, B, and C are constants and

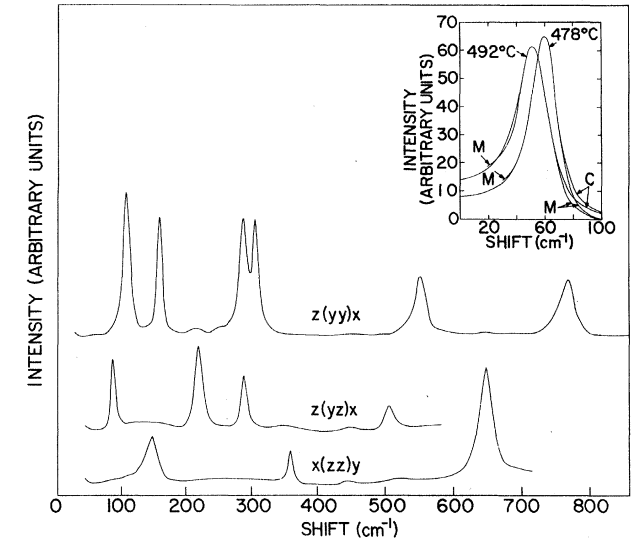

FIG. 1. Some typical spectra for various polarizations of $PbTiO_3$ at 23°C. The bottom curve shows two A_1 transverse-optic modes, A_1(TO). Three are expected. The mode at 150 cm^{-1} does not appear to be a first-order Raman line and the lowest A_1(TO) mode is not directly observed but is seen in the quasimode spectrum. The middle curve shows the expected four E transverse-optic modes. The top curve shows a quasimode spectrum. All the modes that should be observed are present except a longitudinal mode associated with the A_1(2LO) and E(3LO). This mode is possibly the one evident at 440 cm^{-1}. The insert shows the measured (M) and calculated (C) shape of the lowest mode from the middle spectra at high temperatures, E(1TO). The calculated fit is discussed in the text.

T_0 is the Curie temperature, $\Delta F = A(T-T_0)P^2 - BP^4 + CP^6$, one can show[1b,11]

$$\frac{4\pi}{\epsilon_z}=\frac{8}{3}\frac{B^2}{C}\left[(1-\tfrac{3}{4}\tau)+(1-\tfrac{3}{4}\tau)^{1/2}\right], \tag{3}$$

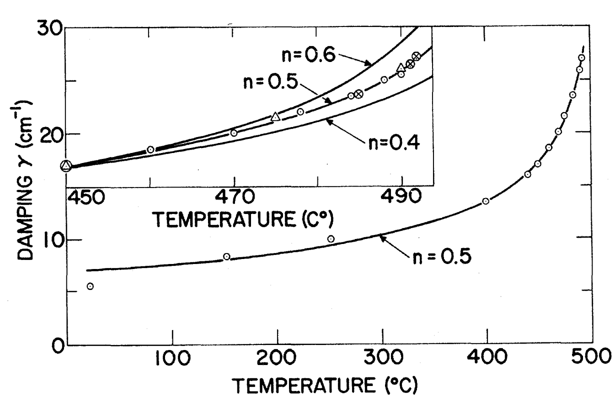

FIG. 2. Measured linewidths, or more exactly, the damping constants [Eq. (2)], versus temperature for the soft E(1TO) mode. The solid line is the calculated curve, fit to the data at 450°C, described in the text.

where $\tau=(T-T_0)/(T_c-T_0)$. This describes $\epsilon_z(T)$ in the ferroelectric phase when P is large. It can be easily shown that ϵ_z in Eq. (3) diverges at a temperature above T_c given by $T_u=T_0+(\frac{4}{3})(T_c-T_0)$. From recent dielectric measurements[12] in $PbTiO_3$, $T_c=493°C$ and $T_0=450°C$, so $T_u=507°C$. Using $\tau=(T-450°C)/43°C$ in Eq. (3), the temperature dependence of γ was calculated assuming $\gamma\propto(\epsilon_z)^n$. The proportionality constant was obtained by fitting at 450°C. Figure 2 indicates that excellent agreement with the experimental points occurs with $n=\frac{1}{2}$. In units of cm^{-1}, $\gamma=(24.1)[(1-3\tau/4)+(1-3\tau/4)^{1/2}]^{-1/2}$ describes this curve.[13]

It should be pointed out that the experimental data shown in Figs. 2 and 3 were taken with increasing temperature. The ferroelectric transition in $PbTiO_3$ is first order with thermal hysteresis. Upon heating, the transition takes place at 495.5°C with an abrupt disappearance of the Raman spectrum as expected from Eq. (2) because P_s goes to zero discontinuously and there are no Raman-active modes in the cubic, high-temperature phase. Upon cooling from the paraelectric state the transition takes place at 488°C. At this temperature the observed line positions and damping constants are identical to those observed on heating at 488°C.

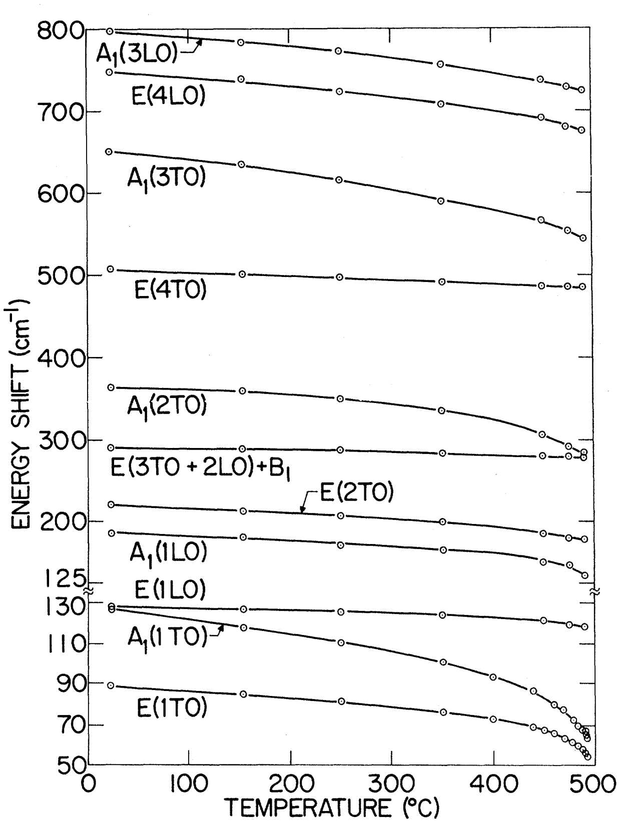

FIG. 3. Temperature dependence of the various Raman lines. Note that the scale is broken at 125 cm^{-1} to clarify the soft modes.

Figure 3 shows the temperature dependence of the observed lines including all the TO and all but two of the longitudinal (LO) modes. All of the TO modes were observed directly, i.e., the E(TO) in $z(yz)x$ scattering and the A_1(TO) in $x(zz)y$ scattering, except the lowest A_1(TO). This mode could only be found by measuring the quasimode ω_{QA} in $z(yy)x$ scattering as in Fig. 1 and determining $\omega_{A_1(\mathrm{TO})}$ from $\omega_{QA}{}^2=\omega_{A_1(\mathrm{TO})}{}^2\sin^2\theta+\omega_{E_1(\mathrm{TO})}{}^2\cos^2\theta$ where $\theta=45°$. This is an approximation[14,15] that we have found to be reasonably good for the other quasimodes where we have measured the A and E transverse mode as well as the quasimode. The longitudinal modes in general were not as intense as the transverse modes. The highest-A and lowest-E longitudinal modes were directly observed in $x+z(yy)x-z$ and $x(yz)y$ polarization, respectively.[8] The quasimodes associated with the highest and lowest longitudinal modes were also observed as in Fig. 1. Thus, the highest-E and lowest-A longitudinal modes were calculated as above for quasimodes. The middle longitudinal mode was not observed with certainty. However, a weak line occurs at 440 cm^{-1}, which is possibly the position of the E and A mode. As discussed below this value was used in the LST equation.

In the ferroelectric phase the low-frequency clamped dielectric constants $\epsilon_z(0)$ and $\epsilon_x(0)$ are related to the A and E modes, respectively, and the optical dielectric constant by the LST relation $\epsilon(0)/\epsilon(\infty)=\prod_i(\omega_{\mathrm{LO}i}/\omega_{\mathrm{TO}i})^2$. The product for for $\epsilon_z(0)$ is taken over the three A modes and for $\epsilon_x(0)$ over the four E modes. Estimating $\epsilon_\infty=5.5$, we calculate that $\epsilon_z(0)$ varies from 26 at 23°C to 95 at 490°C. [For the same two temperatures $\epsilon_x(0)$ varies from 100 to 300.] These values cannot be compared with recent dielectric measurements[12] in $PbTiO_3$ where the free dielectric constant was determined.

The results here can be compared with a brief report of unpolarized Raman work, and polarized infrared work.[5] The Raman results are, in general, similar to those reported here, except for the temperature dependence near T_c, since no sharp dependences were reported.[5] The only other discrepancies are (1) the mode reported[5] at ~150 cm^{-1} does not appear to be a first-order mode as discussed above, and (2) the highest frequency mode reported[5] is a quasimode, also as discussed above. The polarized infrared room-temperature results are in general similar to those reported here. However, the infrared results above T_c are difficult to understand.

The values for the frequencies of $PbTiO_3$ are quite similar to those found for $BaTiO_3$[2-4] and related perovskites.[6] Also we have found no difference in E-mode frequencies propagating in the xy plane or in the z direction. In $BaTiO_3$ one mode is reported to show such a difference.[4]

Lastly, we should compare our observations with those of Shirane, Axe, Harada, and Remeika.[16] They measured by neutron diffraction the lowest mode above T_c and the lowest transverse E and A_1 modes at 22°C, and found these modes to be underdamped. At 22°C they obtain 97 and 148 cm^{-1} for the E(1TO) and A(1TO) modes at the zone center, which compares with 89 and 128 cm^{-1} reported here.

It is a pleasure to acknowledge the technical assistance of F. Dacol and K. H. Nichols and stimulating conversations with Dr. E. Pytte and Dr. B. D. Silverman, and to thank Dr. J. D. Axe for communicating the results in Ref. 16 to us prior to publication.

---

*Work partially supported by the U. S. Army Research Office (Durham).

[1a] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, Oxford, England, 1962).

[1b] E. Fatuzzo and W. J. Merz, *Ferroelectricity* (Wiley, New York, 1967).

[1c] W. Kaenzig, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1957), Vol. 4, pp. 1-197.

[2] L. Rimai, J. L. Parsons, J. T. Hickmott, and T. Nakamura, Phys. Rev. 168, 623 (1968).

[3] A. Pinczuk, E. Burstein, and S. Ushioda, Solid State Commun. 7, 139 (1969).

[4] M. Di Domenico, Jr., S. H. Wemple, S. P. S. Porto, and R. P. Bauman, Phys. Rev. 174, 522 (1968).

[5] C. H. Perry and N. E. Tornberg, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, Berlin, 1969), p. 467, and Phys. Rev. 183, 595 (1969).

[6] For a discussion of some experimental linewidths in perovskites see P. A. Fleury and J. M. Worlock, Phys. Rev. 174, 613 (1968).

[7] M. L. Sholokhovich, Zh. Neorg. Khim. 3, 1214 (1958) [Russ. J. Inorg. Chem. 3, 207 (1958)].

[8] The notation $a(bc)d$ indicates that the laser beam enters the crystal in the crystallographic a direction, polarized in the b direction, and is scattered toward the monochromator polarized in the c direction, traveling in the d direction. See T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev. 142, 570 (1966).

[9] K. Tani, J. Phys. Soc. Jap. 26, 93 (1969).

[10] E. Pytte, Phys. Rev. B 1, 924 (1970).

[11] S. Triebwasser, Phys. Rev. 101, 993 (1956).

[12] J. P. Remeika and A. M. Glass, Mater. Res. Bull. 5, 37 (1970).

[13] The damping coefficient also can be fitted to a form, in cm^{-1}, $\gamma = 65(T_u - T)^{-0.35}$. Actually, one can obtain $(T_u - T)^{-3/8}$ from Eq. (3) by replacing an arithmetic average of two quantities that are close in value by their geometric average.

[14] R. Loudon, Advan. Phys. 13, 423 (1964).

[15] C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, Phys. Rev. 181, 1351 (1969).

[16] G. Shirane, J. D. Axe, J. Harada, and J. P. Remieka, to be published.

ANOMALOUS BETA-ALPHA ANISOTROPY IN THE DECAY OF ^{20}Na†

Neil S. Oakey
Cyclotron Institute, Texas A & M University, College Station, Texas 77843

and

Ronald D. Macfarlane*
Niels Bohr Institute, Copenhagen, Denmark, and Department of Chemistry and Cyclotron Institute, Texas A & M University, College Station, Texas 77843
(Received 14 April 1970)

An anisotropy has been observed in the β-α directional correlation for an allowed β^+ decay in ^{20}Na. The effect is much larger than expected from interference from the second-order "weak magnetism" alone. The possibility of an enhanced $E2$ interference is discussed.

The observation of anisotropies in β-α directional correlations for allowed transitions is one method for studying contributions from high-order matrix elements in β decay. The first positive correlation was reported by Nordberg, Morinigo, and Barnes[1] for the allowed β decay of ^{8}Li and ^{8}B. They found that the contribution from the "weak magnetism" due to the conserved vector current produced a small but measurable anisotropy in the β-α correlation. We report