to be due to the increase of the amplitude and the penetration depth of the electric field inside the metal.

In conclusion it was shown that electromagnetic generation of transverse acoustic waves can be achieved at relatively high temperatures. The conversion efficiency of electromagnetic into acoustic energy was found to be strongly temperature dependent, decreasing with increasing temperatures. The temperature dependence of α is believed to be due to the temperature dependence of the electronic mean free path, l. To explain the experimental data, a theory was developed assuming diffuse surface scattering and including bulk scattering as well. Good agreement was found between theory and experiment, thus showing again that the main mechanism for electromagnetic generation of transverse phonons is diffuse scattering of the conduction electrons at the metal surface.

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Pressure-Induced Phase Transition in Paratellurite (TeO_2)†

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We report a pressure-induced phase transition in paratellurite which occurs at 9.0 kbar at room temperature. The transition appears to be second order and is driven by the soft acoustic mode $\rho V^2 = \frac{1}{2}(C_{11} - C_{12})$ propagating along $\langle 110 \rangle$. This is the only known phonon-driven transition that can be induced with pressure, but not with temperature, for which the details of the transition mechanism have been definitely established. The phase transition was investigated using Brillouin-scattering, ultrasonic-velocity, and dielectric-constant measurements.

Since the introduction of the soft-mode concept[1] for structural phase transitions in solids, there have been numerous attempts[2,3] to find systems which undergo a pressure-induced phase transition driven by a soft acoustic mode. These investigations revealed several materials in which acoustic modes softened with pressure. However, the acoustic mode softenings were only a few percent, and detailed understanding of the pressure-induced phase transitions was complicated by the strong first-order nature of the transitions. The purpose of this Letter is to report a pressure-induced phase transition in paratellurite which is driven by the softening of the $\rho V^2 = \frac{1}{2}(C_{11} - C_{12})$ acoustic mode. As we shall see below, this transition, which occurs at 9.0 kbar at room temperature, appears to be a completely reversible, ideal second-order phase transition.

Large single crystals of high optical quality have been grown for the paratellurite structure of TeO_2 [$D_4(422)$ symmetry], and this material has recently received attention for nonlinear optical, piezoelectric, and acoustoelectric applications. Measurements of the elastic properties[4-7] demonstrate that it has highly anisotropic sound velocities with an anomalously slow shear wave ($V_s = 0.61 \times 10^5$ cm/sec) propagating along $\langle 110 \rangle$ and polarized along $\langle 110 \rangle$. The velocity of this wave is determined by the combination of elastic constants $C' = \frac{1}{2}(C_{11} - C_{12})$ and the low velocity is a result of the near cancelation of C_{11} and C_{12}. Furthermore, the mode softens slightly with decreasing temperature.[5] These previous measurements led us to investigate the pressure dependences of the Raman and Brillouin spectra of paratellurite for evidence of optic-acoustic phonon interactions and a possible pressure-induced phase transition.

We observed no anomalous pressure dependences for the Raman-active modes for pressures up to 4 kbar. Similarly, previous measurements of the temperature dependences of the Raman[8] and infrared[9,10] spectra demonstrated that all of the optic modes display normal temperature dependences. However, our Brillouin scattering measurements revealed that C' softened rapidly with pressure and detailed measurements of the pressure dependences of the ultrasonic velocity, dielectric constants, and Brillouin spectrum demonstrated that paratellurite undergoes a second-order (or very nearly second-order) pressure-induced phase transition at $P_t = 9.0$ kbar at room temperature.

The ultrasonic transit time of the anomalous shear acoustic mode was measured as a function of pressure using a standard pulse-echo technique. The pressure fluid was pentane, and the pressure was measured with a calibrated Manganin coil. Most of the measurements were made at a frequency of 5 MHz, but one run at 2 MHz was also made in an attempt to obtain data as close as possible to the transition pressure where the signal becomes highly attenuated. The samples were single crystals with 6-mm × 6-mm cross sections and thicknesses (along ⟨110⟩) of 2, 4, and 6 mm. Our measured sound velocity for the C' mode at 23°C and atmospheric pressure was 0.615×10^5 cm/sec, in agreement with previous results.[4] The reduced pressure dependence of C' at 23°C is shown in Fig. 1. The data were reduced assuming the axial compressibilities are constant with pressure, which probably does not introduce errors of more than a few tenths of a percent in the results. The velocity decreases with pressure at an initial rate of $\cong -6.5\%$/kbar and the rate of decrease increases with pressure yielding an essentially quadratic $V^2 \propto P_t - P$ behavior. Deviation from this quadratic form, illustrated by the deviation of the reduced elastic constants from linearity, probably results primarily from nonlinear pressure dependences of the individual elastic constants. It can also be seen from Fig. 1 that the acoustic velocity appears to decrease smoothly to zero so that the transition appears to be second order. The smallest value of the reduced constant $C'(P)/C'(0)$ that was measured was 0.005, which was obtained at a pressure of ~0.05 kbar below P_t. The ultrasonic signal could not be seen over a pressure interval of ~0.1 kbar in the vicinity of P_t because of the high attenuation. The transition pressure defined as the center of this interval agrees within

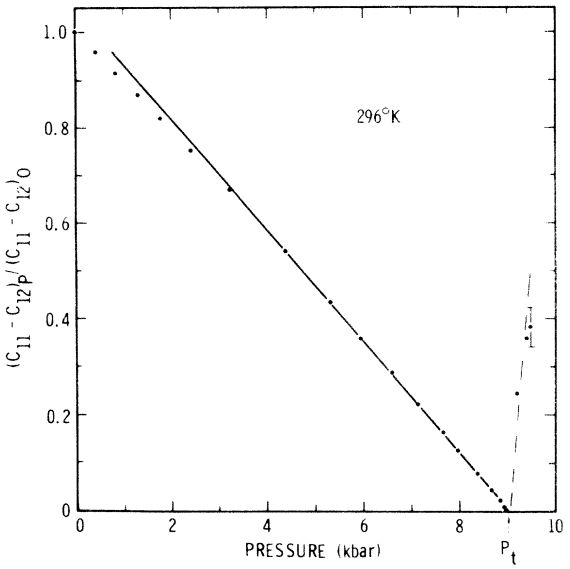

FIG. 1. Pressure dependence for the elastic constants of the soft mode in TeO_2.

experimental error with the pressure at which $C'(P)$ extrapolates to zero.

The acoustic pulse in the high-pressure phase was highly distorted, making it impossible to obtain reliable transit-time data in this phase. The dashed line and three data points for pressures above 9 kbar in Fig. 1 give the approximate behavior of the effective elastic constant in the high-pressure phase. The effective elastic constant in the high-pressure phase, of course, may not be $\frac{1}{2}(C_{11} - C_{12})$; in fact, the experimental configuration may cause more than one mode to be excited in this phase. The measurements are further complicated by the possible existence of a domain structure in the high-pressure phase.

Brillouin-scattering measurements were made on polished single-crystal cubes. The samples were immersed in the pressure fluid and all measurements were taken at a scattering angle of 90°. The source was a single-mode argon laser at a wavelength of 4880 Å, and the scattered light was analyzed with a piezoelectrically scanned Fabry-Perot interferometer with an operating finesse of 45–50.

The Brillouin frequency ω is related to the sound velocity V by[11]

$$\omega = (\omega_0 V/C)(n_i^2 + n_s^2 - 2n_i n_s \cos\theta)^{1/2}, \quad (1)$$

where ω_0 is the laser frequency, θ the scattering angle, and n_i (n_s) the refractive index for the incident (scattered) light. Paratellurite is optically active and birefringent, and the refractive in-

dices have been measured previously.[12,13] We used the refractive indices reported by Singh, Bonner, and Van Uitert[13] of $n_0 = 2.3297$ and $n_e = 2.4951$ at 4880 Å to analyze these data.

A difficulty arises in investigating the soft mode by Brillouin scattering techniques because the scattering cross section vanishes for $\vec{q}$ precisely along $\langle 110\rangle$; thus, for the desired geometry $\vec{k}_i \| \langle 100\rangle$ and $\vec{k}_s \| \langle 0\bar{1}0\rangle$, where $\vec{k}_i$ ($\vec{k}_s$) is the incident (scattered) wave vector, the soft mode was not observed. To study this mode, the sample was rotated about $\langle 001\rangle$ so that $\vec{q}$ was at an angle of 2 to 3° relative to $\langle 110\rangle$. While this rotation allows the soft mode to be observed, it also adds a small contribution to C' from other elastic constants which dominates the sound velocity near the phase transition (see Fig. 2).

The velocities of the three acoustic modes for $\vec{q} \| \langle 110\rangle$ are $V_1^2 = C_{44}/2\rho$, $V_2^2 = (C_{11} - C_{12})/2\rho$, and $V_3^2 = (C_{11} + C_{12} + 2C_{66})/2\rho$. Rotation of $\vec{q}$ about $\langle 001\rangle$ by an angle ψ leaves V_1 invariant but changes V_2 and V_3. In particular, the velocity of the soft mode becomes

$$V_2^2(\varphi) = (1/2\rho)\{C_{11} + C_{66} - [(C_{11} - C_{66})^2 + 4\sin^2(\varphi)\cos^2(\varphi)(C_{12}^2 - C_{11}^2 + 2C_{11}C_{66} + 2C_{12}C_{66})]^{1/2}\}, \quad (2)$$

where $\varphi = \pi/4 - \psi$. Thus, to evaluate the pressure dependence of the soft mode, we also require the pressure dependences of C_{11} and C_{66}. Brillouin-scattering measurements using other crystal orientations yielded $d\ln C_{11}/dP = 1.0\%/\text{kbar}$ and $d\ln C_{66}/dP = 0.50\%/\text{kbar}$. Assuming that the elastic constants vary linearly with pressure and that the transition is second order (i.e., $C_{11} = C_{12}$ at $P = P_t$) yields $d\ln C_{12}/dP = 2.1\%/\text{kbar}$. With these values for the logarithmic pressure derivatives of the elastic constants, the pressure dependence of the Brillouin frequency can be predicted for any angle ψ from Eqs. (1) and (2). The results for $\psi = 3°$ are compared with the measured frequency dependence in Fig. 2. The agreement between the measured and calculated pressure dependence is good for pressures up to ~7 kbar. Above this pressure the calculated frequency dependence deviates slightly from the measured value. This discrepancy probably reflects deviations of the elastic constants from their linear pressure dependence and the fact that changes in the compressibility and refractive index with pressure were neglected. It may also be due in part to a small misorientation of the crystal. Thus, the Brillouin-scattering measurements also indicate that, within experimental uncertainty, the phase transition is second order.

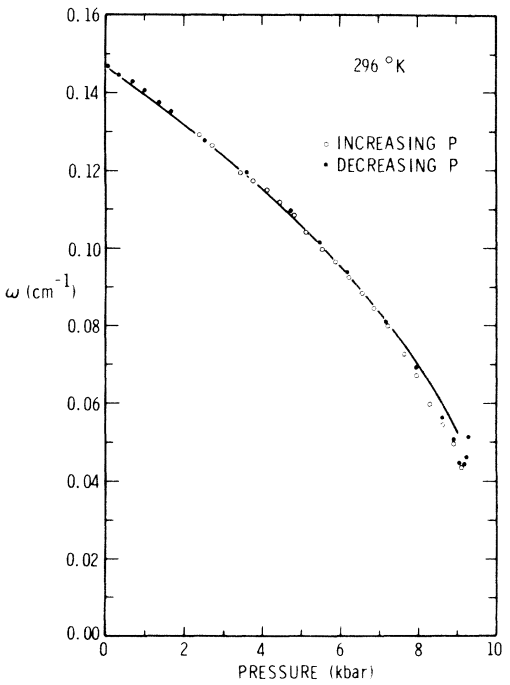

FIG. 2. Pressure dependence of the soft-mode Brillouin frequency in TeO_2 for $\vec{q}$ 3° from $\langle 110\rangle$. Points, measurements of the frequency; solid curve, calculated as described in the text.

To further examine the properties of the phase transition and to determine if the soft acoustic mode is coupled to an infrared-active optic mode, we also measured the pressure dependences of the static dielectric constants. These measurements (see Samara[14] for details) were made on thin (~0.6 mm) a- and c-cut single crystals at a frequency of 10 kHz. The results are shown in Fig. 3.

No dielectric anomaly whatsoever was observed in ϵ_c at the phase transition; rather, ϵ_c decreased smoothly with increasing pressure with an initial rate of $\sim -0.35\%/\text{kbar}$. However, ϵ_a displayed an unusual pressure dependence in that it increased with increasing pressure ($d\ln\epsilon_a/dP \approx 0.25\%/\text{kbar}$) for pressures up to P_t then decreased in the high-pressure phase. Note that the total dielectric anomaly in ϵ_a associated with the phase transition is $<1\%$. This small change in ϵ_a is probably due only to structural changes associated with the transition.

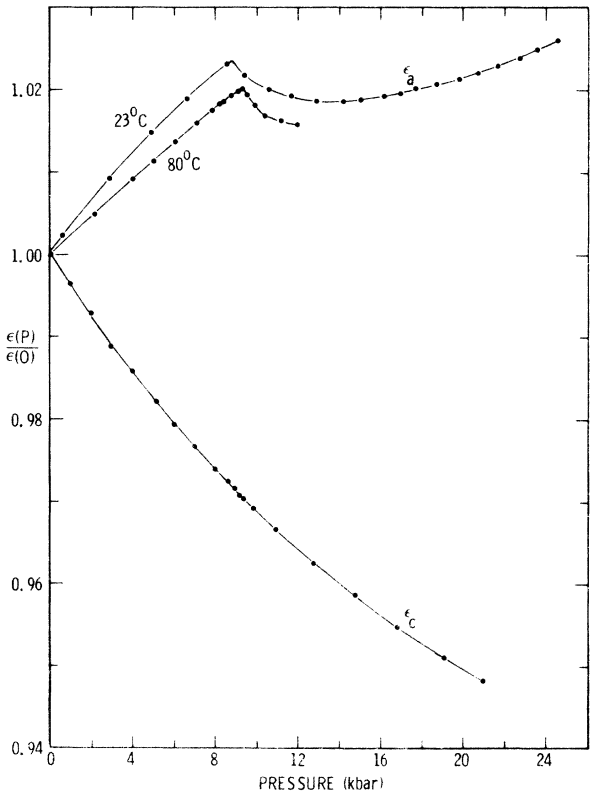

FIG. 3. Normalized pressure dependences of the dielectric constants in TeO_2. The ϵ_c data were taken at 23°C. The lines are guides to the eye.

A second measurement of the pressure dependence of ϵ_a was made at 80°C to determine the slope of the phase boundary in P-T plane. These data are also shown in Fig. 3. At this temperature, the transition pressure is 9.3 kbar which yields $dT/dP_t \approx 190$°K/kbar. Because of the small change in P_t observed between 23 and 80°C, there is a large uncertainty in this slope; however, it is clear that the slope is large and positive. The steepness of the phase boundary is consistent with the fact that no low-temperature transition is observed at atmospheric pressure. In fact, we also found that for $P = 7$ kbar, there is no transition for temperatures to 77°K.

In conclusion, based on the ultrasonic-velocity, dielectric-constant, and Brillouin-scattering measurements, paratellurite undergoes an ideal second-order phase transition at 9.0 kbar which is driven by the soft acoustic mode propagating along ⟨110⟩ described by $\rho V^2 = \frac{1}{2}(C_{11} - C_{12})$. No soft Raman-active modes were observed in the low-pressure phase. This is the only known phonon-driven phase transition that can be induced with pressure, but not with temperature, for which the details of the transition mechanism have been determined. The structure of the high-pressure phase is not known. The lattice distortion produced by the soft shear mode suggests that the high-pressure structure is orthorhombic (D_2). To the authors' knowledge, the only high-pressure structural information available for TeO_2 is the early work by Kalbalkina, Vereshchagin, and Kotilevec,[15] who reported a first-order transition at 30 kbar with an attendant volume change of −7%. While the high-pressure structure they reported is orthorhombic, in agreement with what we speculated, the phase transitions are apparently different. More detailed measurements are required to determine the high-pressure structure.

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