PHYSICAL REVIEW B VOLUME 13, NUMBER 6 15 MARCH 1976

Study of the pressure-induced phase transition in paratellurite (TeO_2)[†]

E. F. Skelton and J. L. Feldman
Naval Research Laboratory, Washington, D. C. 20375

C. Y. Liu* and I. L. Spain
University of Maryland, College Park, Maryland 20742

(Received 17 June 1975)

X-ray measurements have been carried out on paratellurite (TeO_2) at pressures up to 89 ± 1 kbar. Based on both single-crystal and polycrystalline data, a phase transformation from the tetragonal $P4_12_12$ (D_4^4) space group to the orthorhombic $P2_12_12_1$ (D_2^4) space group is observed in the vicinity of 8 kbar; no other pressure-induced transitions have been found. These results are consistent with recent neutron-scattering measurements, but at variance with the only previously reported high-pressure x-ray study of this material. In addition, ambient-pressure single-crystal measurements were performed to temperatures below 10 K with no indication of a low-temperature structural transformation. The pressure dependences of the unit-cell parameters have been determined both above and below the critical pressure P_c. In the orthorhombic phase, the b axis exhibits a negative linear compressibility and the quantity $(b-a)^2/ab$ is found to vary linearly with pressure, extrapolating to zero at 8 ± 1 kbar. Formal theoretical considerations are given for determining the order parameter of this transition and the essential equivalence of other published theoretical treatments is demonstrated. Single-crystal oscillation photographs indicate that in a hydrostatic environment, a domain structure will exist above P_c with strained regions at the domain interfaces which appear to fracture at about 12 kbar. Direct evidence is presented for pressure-dependent atomic motion in the orthorhombic phase. These data can be most easily interpreted in terms of small atomic perturbations in a direction commensurate with the acoustic phonon mode known to be associated with this transition.

I. INTRODUCTION

Tellurium dioxide is a material having three known crystalline forms at standard temperature and pressure (STP). Natural TeO_2 has been found to crystallize in both the rutile and brookite structures of TiO_2, whereas all synthetically prepared TeO_2 forms in a slightly different tetragonal structure known as paratellurite.[1] It is this latter form of TeO_2 which exhibits very interesting pressure dependences of its structural and lattice-dynamical properties. Peercy and Fritz[2] reported that, based on their Brillouin-scattering, ultrasonic, and dielectric-constant measurements, paratellurite undergoes a pressure-induced phase transition at 9 kbar, driven by a soft phonon mode, which appears to be of second order. They further note that this is the only known example of such a transformation which can only be activated with pressure and for which the details of the phase transition are understood.

Ohmachi and Uchida[3] first noted that at STP, paratellurite has an exceptionally slow shear wave propagating in the [110] direction; they also found that the velocity of this wave decreases significantly with decreasing temperature. As viewed from below the critical pressure P_c and based on the work of Peercy and Fritz,[2] this transformation is known to be induced by a softening of the transverse-acoustic phonon wave propagating in the [110] direction and polarized along $[1\bar{1}0]$. The square of the velocity of this particular wave is proportional to the difference between the c_{11} and c_{12} elastic constants, i.e., $\rho v^2 = \frac{1}{2}(c_{11}-c_{12}) \equiv C'$. Peercy and Fritz[2] further observed that the ratio $C'(P)/C'(0)$ varies linearly with pressure extrapolating to zero at 9.0 kbar. On this basis, they suggest that the transition may be of second order.

In addition, Kabalkina, Vereschagin, and Kotilevets[4] reported that paratellurite undergoes a first-order pressure-induced transition. Based on x-ray measurements up to 60 kbar, Kabalkina *et al.* found that at 30 kbar paratellurite transforms from a tetragonal to an orthorhombic structure with an associated 7% reduction in volume. They stated that the high-pressure space group is *Pnnm* (D_{2h}^{12}) and suggested that the structure is similar to that of $CaCl_2$. They further reported a halving of the c axis (and hence of the unit cell) on passing from the tetragonal to the orthorhombic lattice, in addition to a negative linear compressiblity in the c direction in the low-pressure phase. Kabalkina *et al.* made no mention of any other pressure-induced structural transformations in this material.

Several other groups have carried out work on paratellurite concurrently with, and independently of, the present work. Worlton and Beyerlein[5] (WB) initiated experiments on elastic neutron time-of-flight studies shortly before our own studies began. McWhan, Birgeneau, Bonner, Taub, and Axe[6]

(MBBTA) have reported both elastic and inelastic neutron scattering measurements. Both groups as well as Fritz and Peercy[7] (FP) have also introduced phenomenological theories to describe the transition based on Landau[8] order-parameter theory. (See also Anderson and Blount[9] who discussed the case of a strain-induced structural transition.)

Our results on the crystallographic description of the transition are in close agreement with those of SB and MBBTA and all groups observe the transition at ~ 9 kbar in agreement with Peercy and Fritz.[2] In concurrence with WB, we identify the high-pressure orthorhombic phase as belonging to the $P2_12_12_1$ space group, although our arguments are based on group-theoretical considerations.

MBBTA took data with the objective of studying the pressure dependence of the dispersion relations for those phonon modes previously shown to soften at 9 kbar.[2] They found a very small pressure dependence and thus concluded that the softening seen by Peercy and Fritz[2] must be restricted to only the long lattice waves. Fritz and Peercy[10] have also found that none of the optic modes with B_1 symmetry, i.e., those with the correct symmetry for the transition, soften in the low-pressure phase.

The purpose of this paper is to amplify on our earlier reports[11,12] and to provide additional information concerning the phase transition in paratellurite. In this work, x-ray measurements are reported up to pressures of 89 ± 1 kbar and at ambient pressure to temperatures below 10 K. Data have been collected from both single crystals and polycrystalline samples obtained from two different sources. A high-pressure domain structure is observed and the x-ray results are analyzed in terms of symmetry modifications, linear compressibilities, and pressure-dependent atomic motion. Formal theoretical considerations are given for determining the order parameter of this transition and comparison is made with previous theoretical analyses.

II. EXPERIMENTAL PROCEDURES

A. Paratellurite samples

Data were collected from both polycrystalline and single-crystal TeO_2 samples obtained from two different sources. The polycrystalline material was purchased as "ultrapure" from Ventron Corp. Ventron analyses of typical TeO_2 samples supplied under this classification reveal less than 2 ppm each of Fe and Se, and less than 3 ppm of other metals. A least-squares analysis of the measured TeO_2 powder pattern based on a tetragonal lattice yielded the following unit-cell parameters: $a = 4.8092 \pm 0.0025$ Å and $c = 7.6122 \pm 0.0068$ Å. These compare favorably with the published values of 4.810 and 7.613 Å for a and c, respectively.[13] The polycrystalline TeO_2 powder used in this investigation was reground and passed through a 400-mesh sieve.

The single-crystal samples were supplied by Fritz of Sandia Laboratories and came from the same batch used in the aforementioned investigations.[2] The crystals used in this work were generally less than 0.2 mm on an edge and were selected on the basis of good optical and x-ray quality.

B. Pressure generation and measurement

Two types of diamond anvil pressure cells were used: One is fabricated of Be and is similar to the design developed by Weir, Piermarini, and Block[14]; the other is a modified version of the cell used by Bassett, Takahashi, and Stook.[15] The modifications in the latter case relate to improved x-ray collimation and diamond-seating arrangements. Explicit details of the high-pressure x-ray systems will be discussed elsewhere.[16]

In all cases a gasket was used to contain the pressure and for all single-crystal work, and most of the polycrystalline work, a hydraulic fluid was used to fill the pressure cavity—a mixture of 4:1 by volume of methanol : ethanol[17] with a < 10% by volume of added glycerine. A few polycrystalline samples were also run in the absence of a fluid without any appreciable change in the observed compressibilities.

In addition to the sample, a polycrystalline calibrant was also contained in the pressure cavity; NaCl and CsCl were used interchangeably for this purpose. The pressure was computed from the measured shift in the diffraction lines of the calibrant with the aid of the equation of state calculations of Decker.[18] The overall uncertainty in the evaluation of the pressure is estimated to be less than ± 1 kbar and ± 0.5 kbar for the polycrystalline and single-crystal studies, respectively.

C. Data collection Photographic measurements

X-ray data were collected from both the polycrystalline and single-crystal samples by conventional photographic techniques. The pressure cavities were irradiated through the diamond anvils with Zr-filtered radiation from a Mo x-ray tube operated at 48 kV and 14 mA. Exposure times were typically about 15 to 20 h in the case of the polycrystalline studies. Single-crystal data were collected on oscillation photographs recorded with the Be cell mounted on an x-ray diffractometer. The oscillation angle was 30° and little difficulty was experienced in indexing the photographs.

Each pressure run was started at a small positive pressure; this was necessary to seal the cell. Data were recorded at fixed values of pressure at 296 K and each series of photographs was concluded with at least one ambient pressure measurement for purposes of calibration. A correction was applied for the small displacement of the scattering center with increasing load.

The relative positions of the powder lines in the one case, and of the single-crystal reflections in the other, were measured on a semiautomated microdensitometer. The instrumental error in the position determination of the microdensitometer was one micron.

D. Intensity measurements

The relative intensities of selected TeO_2 powder lines were determined as a function of pressure by three different methods. In one case, a polycrystalline sample was contained in the Be cell on the diffractometer and irradiated with Zr-filtered radiation from the Mo x-ray tube. The intensities were measured with a NaI(Tl) detector and associated pulse-height analyzing electronics by step scanning in 2θ through the peaks while, at the same time slowly oscillating in ω so as to optimize the randomness of the TeO_2 particle orientations. The angular increment between steps in 2θ was $\frac{1}{60}°$. Smooth curves were drawn through a plot of the individual data points. In those cases where the resolution of adjacent peaks was not complete, peak overlap was corrected for by assuming the peaks to be symmetric and by subsequent extrapolation. In cases where the peaks were clearly defined, they did appear to be symmetric about their maxima. A linear background correction was applied and the integrated intensities were determined by mechanical integration of the intensity contours with the aid of a planometer.

The intensities were also measured with a Si(Li) energy sensitive detector with a measured resolution of 175 ± 6 eV. In this case, the incident Mo radiation was unfiltered and the data were recorded at fixed 2θ position. The data were collected with a multichannel analyzer set for 67.2 eV per channel resolution. In most cases, the integrated intensities were determined from Gaussian curves fitted to the recorded spectrum with appropriate background corrections.[19] In a few instances, where the separate peak contours were not adequately resolved, the background corrected peak heights were considered.

A third estimate of the relative intensities was made from densitometer tracings of selected powder photographs. Although no effort was made to calibrate the densitometer values in terms of absolute intensities, it was noted that the regions of interest on the films were far from being totally exposed. The integrated intensities were determined by mechanical integration of the densitometer curves. As in the previous meansurements with the polychromatic radiation, in those instances where the peaks of interest were too close to allow adequate resolution, the intensities were determined directly from the peak heights above background.

III. RESULTS AND DISCUSSION

A. Phase transformation

The low-pressure ($P < 8$ kbar) polycrystalline and single-crystal photographs were readily indexed on the basis of the known tetragonal structure. At elevated pressures ($P > 10$ kbar), it was observed that those powder lines with $h \neq k$ split, the amount of splitting being obviously pressure dependent; (*hhl*) lines however did not split. This line splitting was reversible on cycling through the 8–10 kbar region. All the photographs showing the splitting could be indexed on the basis of an orthorhombic lattice. These observations therefore support the conjectures of Peercy and Fritz[2] concerning the probable lattice symmetry of the phase above 9 kbar and the subsequent measurements of WB and MBBTA.

Data were recorded at pressures up to 89 ± 1 kbar. No evidence was found for the first-order transition at ~30 kbar reported by Kabalkina *et al.*[4] even when their experimental conditions were approximately duplicated by squeezing directly onto the mixed sample and calibrant powder. In such experiments the sample environment would be nonhydrostatic. Even so, the second-order transition at 8–10 kbar was still observed. The reason for the discrepancy between this work and that of Kabalkina *et al.*[4] is unclear.

Based on elevated temperature measurements to 80 °C, Peercy and Fritz[2] have reported that the slope of the phase boundary in the P-T plane is $dT/dP_c \simeq +190$ K/kbar. Assuming that the slope does not change significantly at reduced temperatures, one would not expect to initiate this transition at cryogenic temperatures without application of several kbar pressure. We confirm that the transition is not activated at ambient pressure and temperatures below 10 K, i.e., single-crystal oscillation photographs recorded at 296 and < 10 K show no indication of a structural modification nor any significant atomic rearrangements. This observation is consistent with the recent temperature dependent dielectric constant measurements of Peercy, Fritz, and Samara.[20]

B. Compressibilities

Both the polycrystalline and single-crystal photographs were indexed on the bases of a tetragonal lattice below the transition and an orthorhombic lattice above. The procedure was to determine the values of the unit-cell parameters which gave the

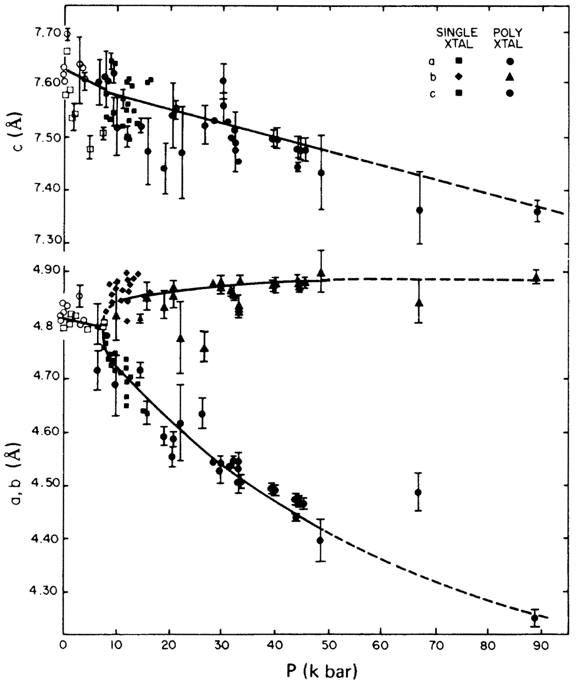

FIG. 1. Pressure dependence of the unit-cell parameters in the tetragonal ($P < 8 \pm 1$ kbar; open symbols) and orthorhombic phase ($P > 8 \pm 1$ kbar; solid symbols).

best least-squares fit to all the data recorded from the same photograph. The resulting unit-cell parameters are plotted versus pressure in Fig. 1; the error bars are computed directly from the least-squares analyses. Data from four different samples, two polycrystalline and two single crystals, are shown in the figure.

The solid curves drawn through the curves in Fig. 1 constitute the best least-squares fit to all the data in the respective structural phases. The measured pressure dependences of the a axis in the tetragonal phase and of the c axis over the entire pressure range are best represented by first-order polynomials. The standard errors of estimate are 0.34% and 0.68% for the a and c axes, respectively, in the tetragonal phase, and 0.60% for the c axis in the orthorhombic phase. The measured pressure dependences of the a and b axes in the orthorhombic structure are more accurately represented by second-order polynomials, the standard errors of estimate being 0.65% and 0.69%, respectively. The curvature of the orthorhombic a and b axes is uncertain below 14 kbar; for this reason, the curves are shown dashed in this region. Similarly, the amount of data above 50 kbar is limited and the curves are shown dashed in the higher-pressure regions also.

Within the common pressure range ($P \leq 20$ kbar), the values of $a(P)$ and $b(P)$ reported here are in agreement with the elastic neutron scattering measurements of MBBTA; we also agree with the unit-cell parameter values determined by WB up to their pressure limit of 32.5 kbar.

The linear compressibilities in the tetragonal phase, k_a and k_c, can be estimated from our low-pressure data: although our experimental uncertainty is large in this instance, approximate values are 5×10^{-4} and 6×10^{-4} kbar^{-1}, respectively. These results can be compared with the linear compressibilities determined from the elastic constant data of Ohmachi and Uchida,[3] viz., $(8.10 \pm 0.39) \times 10^{-4}$ kbar^{-1} and $(6.11 \pm 0.56) \times 10^{-4}$ kbar^{-1} for k_a and k_c, respectively. Excellent agreement is seen between the linear compressibilities in the c direction and, although the value of k_a determined from the elastic constant data is substantially greater than that determined from the x-ray measurements, this difference is probably within our experimental uncertainty. Neither the results reported here, nor those of other workers,[3,5,6] confirm the negative compressibility observed in the tetragonal c direction by Kabalkina *et al.*[4] The reason for this discrepancy is again unclear.

One of the most important features of our results concerns the pressure dependence of the a and b lattice parameters in the orthorhombic structure. Based on the polynomials representing the $a(P)$ and $b(P)$ curves, we find that in the pressure range $14 < P < 22$ kbar, the quantity $[(b-a)^2/ab]$ $(\equiv \eta^2)$ varies linearly with pressure. [Our determination of the curvature of $a(P)$and $b(P)$ below 14 kbar is uncertain; above 22 kbar the slope of the $\eta^2(P)$ curve exhibits a gradual increase.] Section III D and a simple extension of C shows that: η is a suitable order parameter for discussion of this phase transition and; in view of the linearity found in $C'(P)/C'(0)$ for $P < P_c$ (Ref. 2), η^2 is expected to vary linearly with pressure for $P > P_c$. In the linear region, η^2 is represented by the equation $\eta^2 = (2.0 \times 10^{-4}\ \text{kbar}^{-1})\,P - 1.6 \times 10^{-3}$. Assuming that this linear relation is maintained down to the critical pressure, we report that $P_c = 8 \pm 1$ kbar, where the error is estimated from the uncertainty in our measurement of the pressure. This is in agreement with the 9-kbar value reported by Peercy and Fritz.[2]

We note that the other groups previously mentioned also report functions of a and b which exhibit linear pressure dependences: MBBTA plot $(a/b-1)^2$, whereas WB consider $[(b-a)/a_0]^2$. Experimentally, there is little difference among the parameters considered and in the following we adopt yet another definition, used by WB, for η.

C. Theoretical considerations of the transition

Each of the aforementioned groups working on paratellurite (MBTTA, WB, and FP) have developed phenomenological expressions involving order parameters to describe the transition. Although differences may appear to exist in these previous treatments, we shall demonstrate that the various expressions previously developed are essentially equivalent and, in so doing, present a more rigorous treatment of the problem and clarify certain aspects of the previous treatments. Moreover, the phenomenological expressions developed in this section could also be useful, not only for determining the order parameter, but also for evaluating the discontinuities in both the c-axis linear compressiblity and the basal plane compressibility through the phase transition.

Previous approaches to this problem have been as follows: FP and WB each started with a strain-energy involving expansion from an unstable tetragonal state at the pressure of interest (i.e., $P > P_c$) and considered only quadratic and higher-order strain terms. They then proceeded to minimize the strain energy with respect to the strain, which they associated with primary- and secondary-order parameters. There were small differences in the approaches used by these workers: most notably WB included terms in c-axis strain, while FP neglected such terms but expanded to higher orders in basal strains. On the other hand MBBTA set up a strain energy expansion about the $P=0$ state and obtained three equilibrium equations for the pressure, the solution of which yielded an expression for the strains from their initial state.

Starting with the basic expression of MBBTA for the equilibrium conditions (although we do not follow their approach in detail), it will be shown that the minimization conditions of WB and FP result. The pressure is defined as follows[21]:

$$p = -T_i = -\frac{V_0}{V}\left(\frac{\partial u_M}{\partial \nu_i}\right)_{\bar{\nu}=0} \quad (i=1,2,3), \tag{1}$$

where u_M is the strain energy density considered by MBBTA, V_0 and V are the equilibrium volumes at zero pressure and p, respectively, and the ν_i represent strains from the finite pressure equilibrium configuration. This expression reduces to Eq. (4.6) of Barron and Kein[21] if it is noted that $V_0 u_M = W(\bar{\nu}) - W_0$ where $W(\bar{\nu})$ is the energy of the strained state and W_0 that of the zero pressure equilibrium state. Either free (Helmholtz) or internal energies are considered depending on whether isothermal or adiabatic changes, respectively, are made in performing the derivatives of Eq. (1).

Clearly, Eq. (1) remains unchanged if $V_0 u_M$ is replaced by $W(\bar{\nu}) - W_T$ where W_T is the appropriate energy (free or internal) associated with the tetragonal state (which is unstable for $P > P_c$) at the pressure of interest and, by definition, is independent of $\bar{\nu}$. Thus, Eq. (1) becomes

$$p = -\frac{1}{V}\left(\frac{\partial(W(\bar{\nu}) - W_T)}{\partial \nu_i}\right)_{\bar{\nu}=0} \quad (i=1,2,3). \tag{2}$$

For a general strained state W may be considered to depend on all the unit-cell parameters. In view of the fact that only diagonal components of the strain tensor $\nu_i (i=1,2,3)$ must be considered in Eqs. (1) and (2), we may consider the energy in any strained state of interest to be a function of the lattice parameters a, b, and c along the three Cartesian crystallographic axes. We note that a, b, and c depend linearly on ν_1, ν_2, and ν_3, respectively. Next we note that a change of variables to ab, $a-b$, and c allows us to write the expansion

$$W(a,b,c) = W_0(ab,c) + \tfrac{1}{2} W^{\mathrm{II}}(ab,c)\,\Gamma^2 + \tfrac{1}{24} W^{\mathrm{IV}}(ab,c)\,\Gamma^4 + \cdots, \tag{3}$$

where

$$\Gamma \equiv (b-a). \tag{3a}$$

Our choice of variables is governed by their simple transformation properties, i.e., Γ transforms as B_1 and ab and c both transform as A_1 with respect to the tetragonal point group operations, and by the simplicity of our following derivation based on them. No odd terms in Γ appear in Eq. (3) because of the required invariance of W with respect to the tetragonal symmetry operations.

The tetragonal state of interest is determined by Eq. (2) with b set equal to a, or upon use of Eq. (3),

$$p = -\frac{1}{V}\left(\frac{\partial W_0(ab,c)}{\partial \ln(ab,c)}\right)_{a=b}, \tag{4}$$

where the relations, $\nu_1 = da/a$, etc., were also used. Writing the solutions to Eq. (4) as a_T and c_T it is also apparent that $W_T = W_0(a_T^2, c_T)$.

Next upon writing a, b, and c in Eq. (3) as $a_T + \Delta a$, $a_T + \Delta b$, and $c_T + \Delta c$, the following expansion is obtained:

$$\begin{aligned} W - W_T = {} & -p\Delta V + \frac{1}{2!}\frac{\partial^2 W_0}{\partial(ab)^2}[\Delta(ab)]^2 + \frac{1}{2!}\frac{\partial^2 W_0}{\partial c^2}(\Delta c)^2 \\ & + \frac{\partial^2 W_0}{\partial(ab)\,\partial c} + p\,\Delta(ab)\,\Delta c + \frac{1}{2!} W^{II}(a_T, c_T)\,\Gamma^2 \\ & + \frac{1}{2!}\frac{\partial W^{II}}{\partial(ab)}\Delta(ab)\,\Gamma^2 + \frac{1}{2!}\frac{\partial W^{II}}{\partial c}(\Delta c)\,\Gamma^2 \\ & + \frac{1}{24!} W^{IV}(a_T^2, c_T)\,\Gamma^4 + \cdots, \end{aligned} \tag{5}$$

where $\Delta V = abc - a_T^2 c_T$ and where Eq. (4) was used. It should also be understood that the derivatives appearing in Eq. (5) are evaluated in the tetragonal state. Equation (5) can be written in the form:

$$W - W_T = -p\Delta V + V_T u_{\mathrm{WB}}(S_1, S_2, \eta), \tag{6}$$

where u_{WB} is identified as the strain energy term used by WB which is defined by comparing Eqs. (5) and (6) and where we use the following notation:

$$\Delta(ab)/a_T^2 = S_1, \tag{6a}$$

$$\Gamma^2/a_T^2 = \eta^2, \tag{6b}$$

$$\Delta c/c_T = S_2. \tag{6c}$$

It is clear from Eq. (6) that u_{WB} represents the change in the Gibbs function (iosthermal case) or enthalpy (adiabatic case) between the orthorhombic state and the unstable tetragonal state at the same pressure for $p > p_c$.

Two minor differences between the expression for u_{WB} used by us and that used by WB and FP should be mentioned. The first is that we have not ignored terms linear in p as the other authors apparently have done. Additional terms linear in p will appear upon expressing the coefficients of the strains in Eqs. (5) and (6) in terms of the tetragonal state elastic constants.[21] The magnitudes of these terms near the transition pressure are probably about 10% of the corresponding elastic constant terms. In addition our parameter S_1 differs from the corresponding strain parameter $\epsilon_1 + \epsilon_2$ of WB and FP by the term $(\epsilon_1\epsilon_2)$ which is clearly negligible near the transition pressure (here ϵ_1 and ϵ_2 describe basal plane strains of the tetragonal state) and hence there is no significant difference among the WB, FP, and our choice of parameters.

Next, the equation of state is considered. Substituting (5) into (2) yields for $i = 1, 2$, respectively,

$$p = p - \frac{V_T}{V}\left[\frac{ab}{a_T^2}\left(\frac{\partial u_{\mathrm{WB}}}{\partial S_1}\right)_{S_2,\eta} - \frac{a}{a_T}\left(\frac{\partial u_{\mathrm{WB}}}{\partial \eta}\right)_{S_1,S_2}\right], \tag{7}$$

$$p = p - \frac{V_T}{V}\left[\frac{ab}{a_T^2}\left(\frac{\partial u_{\mathrm{WB}}}{\partial S_1}\right)_{S_2,\eta} + \frac{b}{a_T}\left(\frac{\partial u_{\mathrm{WB}}}{\partial \eta}\right)_{S_1,S_2}\right]. \tag{8}$$

Clearly, these equations lead to

$$\left(\frac{\partial u_{\mathrm{WB}}}{\partial \eta}\right)_{S_1,S_2} = \left(\frac{\partial u_{\mathrm{WB}}}{\partial S_1}\right)_{\eta,S_2} = 0. \tag{9}$$

Setting $i = 3$ and using (9), we find in a similar manner

$$\left(\frac{\partial u_{\mathrm{WB}}}{\partial S_2}\right)_{S_1,\eta} = 0. \tag{10}$$

We mention that the same result is obtained with the replacement of S_1 by $(\epsilon_1 + \epsilon_2)$.

Both sets of workers WB and FP obtained specific solutions for the discontinuities in compressiblilities. The present analysis can also give such values. However, in calculating specific values for these quantities, values for the second- and higher-order elastic constants are needed near $p = p_c$. Accurate data on the uniaxial stress dependence of $c_{11} - c_{12}$ would be particularly helpful in calculating these discontinuities. In the absence of these data, no numerical considerations are made.

D. Group-theoretical considerations

Our analyses in this section mainly follow Birman's treatment of second-order transitions.[22] We note that, if this is indeed a second-order transition, then in the Landau theory[8] the crystal space group in the less symmetric phase will be a subgroup of the more symmetric space group. The space group of the low-pressure structure is known to be $P4_12_12$ (D_4^4) (Ref. 1). As tabulated in the *International Tables for X-Ray Crystallography*,[23] there are six subgroups of the $P4_12_12$ (D_4^4) space group. Based on our x-ray data, the less symmetric phase in this case is orthorhombic; only two of the aforementioned six subgroups, $P2_12_12_1$ (D_2^4) and $C222_1$ (D_2^5), correspond to orthorhombic lattices.

An additional condition for this transition to be second-order is that a nonidentity representation of the point group of the low-pressure structure subduce the identity representation of the point group of the high-pressure structure. The point group D_4 of the space group D_4^4 has four one-dimensional representations: A_1, A_2, B_1, and B_2; and one two-dimensional representation: E (Ref. 24). Of the subgroups D_2^4 and D_2^5, the first corresponds to a loss of the two diagonal symmetry axes and the second to a loss of the x and y directional axes of the group D_4^4. It can then be shown that only the identity representation A_1 and the representation B_1 of D_4 subduce the identity representation of the point group of D_2^4 and only A_1 and B_2 of D_4 subduce the identity representation of the point group of D_2^5. Therefore there exists in this case a one-to-one correspondence between the possible group representation associated with the transition and the less symmetric space group. Finally, we note that the order parameter for this transition, i.e., $\epsilon_1 - \epsilon_2$, as evident from the work of Peercy and Fritz,[2] has transformation properties associated with B_1 and therefore on this basis the less symmetric phase must have the D_2^4 space group.

This selection of the space group in the less symmetric phase and hence, from the above, the necessary transformation properties of the order parameter is further confirmed by the fact that the alternate choice, viz., $C222_1$ (D_2^5) corresponds to a c-face-centered lattice which, in turn, requires the absence of all reflections for which $(h+k)$ is odd. These reflections were seen in both the single-crystal and polycrystalline measurements. Our conclusion with regard to the symmetry species involved in the transition and the high-pressure structure is also in agreement with that of Worlton and Beyerlein.[5] However, we disagree with the arguments which are used in their characterization of the strain symmetry, i.e., since the strain in the presence of two degenerate normal modes is a sum of strains, use of a product representation seems physically unreasonable.

E. Domain structure

The high-pressure single-crystal oscillation photographs revealed an interesting feature of this transition. The line splitting observed in the powder photographs is attributed to the tetragonal-to-orthorhombic distortion and, of course, will manifest itself on the oscillation photographs in terms of relatively different displacements for different (hkl) reflections. However, in fact, it was found that within a few kilobars above P_c, a distinct pressure dependent splitting was observed in all (hkl) reflections where $h \neq k$, whereas the (hhl) reflections did not split. For the higher-order reflections ($2\theta > 25°$), and the $K\alpha_1 - K\alpha_2$ doublet was resolved on the oscillation photographs and the splitting seen in these higher-order reflections was present in both members of the doublet. If one member of a split reflection pair was indexed as (hkl), the other was found to correspond to (khl). As long as the sample pressure remained within a few kilobars of P_c, this splitting was completely reversible. It was also reproduced in more than one crystal. It was further observed that, if the pressure in the chamber was increased above 12 kbar, then (i) the splitting was no longer reversible and (ii) the remaining, previously unsplit, reflections also divided irreversibly.

Our interpretation of these observations is as follows: in the high-pressure phase paratellurite may be referred to as being "ferroic" in that it has two stable orientation states in the absence of an applied stress, cf. Ref. 25. Thus, we suggest that, on passing from the prototypic phase through the critical pressure, the selection of orientation state, i.e., which of the two equivalent a axes in the tetragonal phase is to form the new b axis in the orthorhombic phase, is made arbitrarily at each of the various nucleation sites. Therefore, above the critical pressure, the original single crystal is subdivided into domains which are related to one another by an interchange of a-b axes. Clearly, since the linear compressibility of the a axis is positive whereas that of the b axis is negative (see Fig. 1), the strain at the interface between the domains will exhibit a strong pressure dependence. We suggest that above 12 kbar, the elastic limit is exceeded at the interface and permanent fracture results, leading to the irreversible splitting.

This explanation is partially confirmed by visual observations and subsequent microphotographs. Under microscopic examination it was clear that, what had originally been a region of uniform optical transparency, after pressurization above about 12 kbar showed several smaller optically uniform regions, separated by regions of varying transparency, thus suggesting the presence of several crystallites in the cell. It is conjectured that, if a small bias were applied in the prototypic phase and maintained through the transition, e.g., a small uniaxial strain in a [100] direction, then the same orientation would be selected at all nucleation sites and a single crystal would be preserved into the orthorhombic phase. It is noted that Peercy and Fritz[2] suspected the existence of a domain structure in the high-pressure phase. It is unclear however why McWhan *et al.* did not observe a similar phenomenon in their hydrostatic measurements. They do report an increase in the crystal mosaicity with repeated pressure cycling, but apparently their single crystal remained intact up to 20 kbar.

F. Internal atomic motion

It was noted in a number of high-pressure powder photographs that, in additon to the tetragonal-to-orthorhombic line splitting, there was an apparent pressure dependent intensity variation between certain split pairs, viz., (012, 102) and (122, 212). Interpretation of these observations is complicated somewhat by the fact that in each case, there is an additional line which cannot be distinguished from the lower angle member of each pair, i.e.. even at elevated pressures, the (111) and the (004) lines are unresolved from the (012) and (112) lines, respectively. Despite this fact however, it is apparent that the intensity ratios of $(I_{012}+I_{111})$ to I_{102} and $(I_{122}+I_{004})$ to I_{212} both increase with increasing pressure. Such effects can be most simply understood in terms of atomic displacements within the unit cell.

In consideration of the significance of these intensity variations, an effort was made to quantitatively characterize the pressure dependence. Attention was focused exclusively on the (122, 212) pair because it could be more easily resolved due to its larger diffraction angle. The three methods used to assess the intensities have been discussed above. We note that, in those instances where (because of the inadequate resolution of the (212) peak from the (122+004) pair) the peak maxima were used instead of the integrated intensities, the resulting intensity ratios represent a lower estimate of the true integrated intensity ratio. Although there is some scatter in the various measurements, the data, which have been corrected for both Lorentz and polarization effects, yield a measured intensity ratio R_{meas} which increases from a value in excess of 1.4 near 20 kbar to something above 1.8 at 40 kbar. (Because of the close proximity in 2θ of the lines under consideration, an absorption correction was believed to be unnecessary.)

The implications of this intensity variation have been considered in terms of the internal atomic coordinates. Because the x-ray scattering factor of the O atoms is so much smaller than that for the Te atoms, e.g., $(2f_0/f_{\mathrm{Te}})^2 \approx 0.05$ in the region of interest, it is clear that R_{cal} [$\equiv (8I_{122}+2I_{004})/8I_{212}$] will be most responsive to small displacements of the Te atoms. Moreover, we note that the (002) reflection, which is forbidden in the tetragonal structure, is not observed, even at the highest pressures; this suggests that any possible Te-atom displacements in the [001] direction, and associated variations in I_{004}, are probably small.

Starting with the STP atomic positional parameters as specified in Ref. 1, the intensity ratio R_{cal} has been evaluated for a large number of small positional perturbations of both the Te and O atoms. Generally, it is found that the greatest variation in R_{cal} is effected by displacing the Te atoms in the $[1\bar{1}0]$ direction, i.e., this is the smallest structural modification which gives results consistent with our experimental observations. This is also consistent with the softening of the shear constant C'.

By way of comparison, we note that Worlton and Beyerlein[5] concluded, from their elastic neutron scattering data, that the O atoms undergo large displacements through the transition, whereas the motion of the Te atoms is comparatively small. Based on our limited intensity data, we are not in a position to refute this. However, we do find that, based on their results, R_{cal} increases from 1.28 at 8 kbar to 1.34 at 19.8 kbar. The latter value is slightly below our minimum estimate of 1.4 at 20 kbar.

In view of the fact that we, as well as Worlton and Beyerlein, find there are internal displacements associated with this transition it is clear that some coupling exists between the B_1 type elastic strain and some of the five B_1 zone center optic modes.[26] Thus, on the basis of this evidence alone there is a possiblity that an optic mode helps drive the transition through a decrease of its frequency with pressure. However, Raman scattering measurements show that there is no softening of the B_1 optic modes with application of pressure and hence the optic modes do not play an important role in the transition.[10,20]

IV. CONCLUSIONS

We note that at 8 ± 1 kbar, paratellurite transforms from its known tetragonal $P4_12_12$ (D_4^4) space group to the orthorhombic $P2_12_12_1$ (D_2^4) space group. The linear compressiblity of the b axis in the high-pressure phase is negative and the quantity $(b-a)^2/ab$ varies linearly with pressure extrapolating to zero at 8 ± 1 kbar. This linear relationship supports the idea that this is a second-order phase transition. These results are consistent with recent neutron scattering measurements on paratellurite, but at variance with the only previously reported high-pressure x-ray study of this material. Specifically, we do not support the first-order transition reported by Kabalkina *et al.*[4] at 30 kbar. We demonstrate the essential equivalence of published theoretical treatments of this phase transition. In the presence of a hydrostatic pressure environment above the critical pressure we find that a single crystal will subdivide into a number of smaller crystallite domains of alternating a and b axes and further that the strained, noncrystalline interdomain regions will fracture at pressures in excess of about 12 kbar. Finally, we find that there is atomic motion within the unit cell above the critical pressure.

ACKNOWLEDGMENTS

We would like to thank Dr. Weber of Bell Laboratories for a helpful discussion, Dr. I. J. Fritz of Sandia Laboratories for supplying the single crystals used in this work, and D. Vvedensky of the University of Maryland for assistance with some of the calculations. One of us (C. Y. L.) also wishes to thank the National Aeronautics and Space Administration, Lewis Research Center, for a Research Assistantship.

---

[*] Work performed by one of the authors (CYL) in partial fulfillment of the requirements for the degree of Ph. D. from the University of Maryland.

[†] Present address: Communication Systems Division, IBM, Manassas, Va.

[1] R. W. G. Wyckoff, *Crystal Structures*, Vol. I (Interscience, New York, 1963).

[2] P. S. Peercy and I. J. Fritz, Phys. Rev. Lett. 32, 466 (1974).

[3] Y. Ohmachi and N. Uchida, J. Appl. Phys. 41, 2307 (1970).

[4] S. S. Kabalkina, L. F. Vereschagin, and A. Kotilevets, *Seventh International Union of Crystallography*, Moscow, U.S.S.R., 1966, pp. A207–A208 (International Union of Crystallography, Netherlands, 1966).

[5] T. G. Worlton and R. A. Beyerlein, Phys. Rev. B 12, 1899 (1975).

[6] D. B. McWhan, R. J. Birgeneau, W. A. Bonner, H. Taub, and J. D. Axe, J. Phys. Lond. C 8, L81 (1975).

[7] I. J. Fritz and P. S. Peercy, Solid State Commun. 16, 1197 (1975).

[8] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), pp. 430–456.

[9] P. W. Anderson and E. I. Blount, Phys. Rev. Lett. 14, 217 (1965).

[10] I. J. Fritz and P. S. Peercy (private communication, July, 1975).

[11] E. F. Skelton, C. Y. Liu, and I. L. Spain, ACA Program Abst. 2, 259 (1974).

[12] E. F. Skelton, J. L. Feldman, C. Y. Liu, and I. L.

Spain, Bull. Am. Phys. Soc. 20, 557 (1975).

[13] A. S. T. M. X-Ray Powder Data File: Card No. 11–693 (unpublished).

[14] C. D. Weir, G. J. Piermarini, and S. Block, Rev. Sci. Instrum. 40, 1133 (1969).

[15] W. A. Bassett, T. Takahashi, and P. W. Stook, Rev. Sci. Instrum. 38, 37 (1967).

[16] C. Y. Liu, Ph. D. dissertation (University of Maryland, 1975) (unpublished); C. Y. Liu, E. F. Skelton, and I. L. Spain (unpublished).

[17] G. J. Piermarini, S. Block, and J. D. Barnett, J. Appl. Phys. 44, 5377 (1973).

[18] D. L. Decker, J. Appl. Phys. 42, 3239 (1971).

[19] W. Zimmerman, Rev. Sci. Instrum. 32, 263 (1961).

[20] P. S. Peercy, I. J. Fritz, and G. A. Samara, J. Phys. Chem. Solids 36, 1105 (1975).

[21] T. H. K. Barron and M. L. Klein, Proc. Phys. Soc. Lond. 85, 523 (1965).

[22] J. L. Birman, Phys. Rev. Lett. 17, 1216 (1966).

[23] *International Tables for* X-*Ray Crystallography*, Vol. 1, edited by N. F. M. Henry and K. Lonsdale (Kynoch, Birmingham, England, 1952), p. 538.

[24] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[25] K. Aizu, J. Phys. Chem. Solids 32, 1959 (1971).

[26] A. S. Pine and G. Dresselhaus, Phys. Rev. B 5, 4087 (1972).