

Structural parameters for the suspected pressure-induced electron transition in InBi

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Lattice parameters and atomic positions for InBi have been measured at pressures up to 25.6 kbars by time-of-flight neutron powder diffraction. The structure remains tetragonal ($P4/nmm$). However, the compression along the a direction is largest at low pressures and exhibits a broad minimum around 14 kbars which appears to be accompanied by a change in the pressure dependence of individual In-Bi and Bi-Bi nearest-neighbor distances. These observations are consistent with a pressure-induced electron transition involving the disappearance of a hole pocket upon increasing pressure.

INTRODUCTION

Indium bismuthide (InBi) is a metallic III-V compound which crystallizes in the tetragonal $B10$ PbO-type structure rather than the cubic zinc-blende $B3$ structure common for semiconducting III-V compounds. The structure (space group $P4/nmm$) consists of layers of like atoms in planes perpendicular to c , as shown in Fig. 1.¹ The In atoms are located at the origin and at the centers of the square faces (special positions $2a$), while the Bi atoms lie on the other four faces in positions $(0, \frac{1}{2}, z)$, $(\frac{1}{2}, 0, z)$ (special positions $2c$), with $z = 0.393$, and form a corrugated double layer. The interatomic distances in InBi correspond to the sum of the metallic radii and are appreciably larger than the values expected for a covalently bonded or ionic structure.¹ This weak bonding, especially between adjacent Bi-Bi layers, leads to rather anisotropic mechanical properties, including easy cleavage normal to the c direction, and a compressibility along c an order of magnitude larger than perpendicular to c .^{2,3}

A renewed interest in the effect of pressure on InBi began in 1975 when Rapoport, Pitt, and Saunders reported observing an abrupt jump in the resistivity around 19 kbars and suggested that a first-order structural transition may be the cause.⁴ Their result was in general agreement with Bridgman who had reported a "very obtuse cusp with downward break" in the resistivity around 15 kbars.⁵ However, volume compressibility and x-ray diffraction data taken on InBi by Gordon and Deaton had indicated no volume discontinuity or phase change up to 30 kbars,⁶ and Laukhin *et al.* had failed to detect any significant sudden changes in the electrical resistivity of InBi in the range 0–100 kbars.⁷ Nevertheless, Rapoport *et al.* proposed that the transition they observed may involve the merging of the two Bi

layers to form an ordered face-centered tetragonal structure. Such a proposal seemed generally consistent with the large compressibility along c compared to a .

In an attempt to clarify whether or not any structural phase transitions occur in the range 0–25 kbars, Fritz performed high-pressure ultrasonic measurements on single crystals of InBi under hydrostatic conditions.³ He found no "ordinary" phase transitions. In particular, no first-order phase transition was observed and no mechanical instabilities resulting from mode softening were present. However, Fritz did observe unusual acoustic-mode anomalies at high pressure leading to a pronounced minimum in the compression along a in the region of 15 kbars, with the compressibility at this pressure being only about one-third of the atmospheric-pressure value.

The most consistent explanation of the "transition" in InBi has been offered by Schirber and Van Dyke as a result of their high-pressure de Haas-van Alphen (dHvA) measurements and band calculations.⁸ They observed one dHvA frequency with an unusually large negative pressure dependence. Their data extended to 4 kbars in solid He at ~ 1.1 K. A straight-line extrapolation of the data predicts that the α frequency would vanish at about 12.6 kbars. This would give rise to an electron transition of the kind described by Lifshitz⁹ resulting from the disappearance of a region of the Fermi surface upon increasing pressure. Unfortunately, Schirber and Van Dyke's calculated energy-band structure was not compatible with the experimentally known information about the Fermi surface. However, by making some relatively minor band shifts, they were able to propose an energy-band model which was consistent with experiment. A very attractive feature of their model is that the bands show a sufficiently large dependence on c/a (which changes markedly

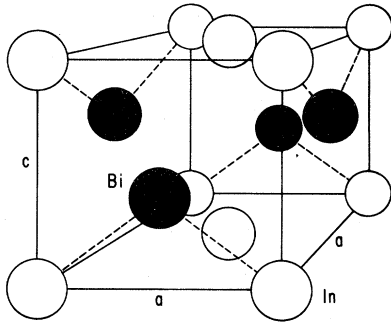


FIG. 1. The tetragonal structure of InBi.

with pressure due to the very anisotropic compressibility) to result in the disappearance of a small hole pocket upon increasing pressure.

The purpose of this paper is to report the first detailed structural measurements on InBi at high pressures and to compare the results with previous work. Time-of-flight neutron powder diffraction overcomes the problems of doing x-ray diffraction from such high- Z atoms, and the ability to perform a full Rietveld profile refinement of the data allows the measurement of small symmetry distortions^{10,11} and the accurate determination of individual atom positions.¹² Thus,

this technique offers the most accurate direct structural method of detecting a structural phase transition and also allows any anomalous pressure dependence of individual atom-atom distances associated with an electron transition to be measured.

EXPERIMENT

Powdered InBi, along with CsCl (pressure calibrant) and Fluorinert FC-75 liquid (3M Company), were sealed in a Teflon capsule and placed in the supported piston cylinder pressure cell described previously.¹² Data were collected on the H-8 time-of-flight powder diffractometer at Argonne's CP-5 research reactor.^{11,12} This instrument uses a large time-focused bank of ^3He detectors (upgraded from BF_3 detectors in 1977) at a fixed scattering angle of $2\theta = 90^\circ$ to give high count rates at a nominal resolution of $\Delta d/d = 0.012$ for $d = 1 \text{ \AA}$. Data were collected for about 48 h at each pressure.

The data were analyzed using a multicomponent profile refinement technique¹³ in which a calculated diffraction profile is least-squares fitted to the raw data with the lattice parameters, atomic position, and temperature factors being the vari-

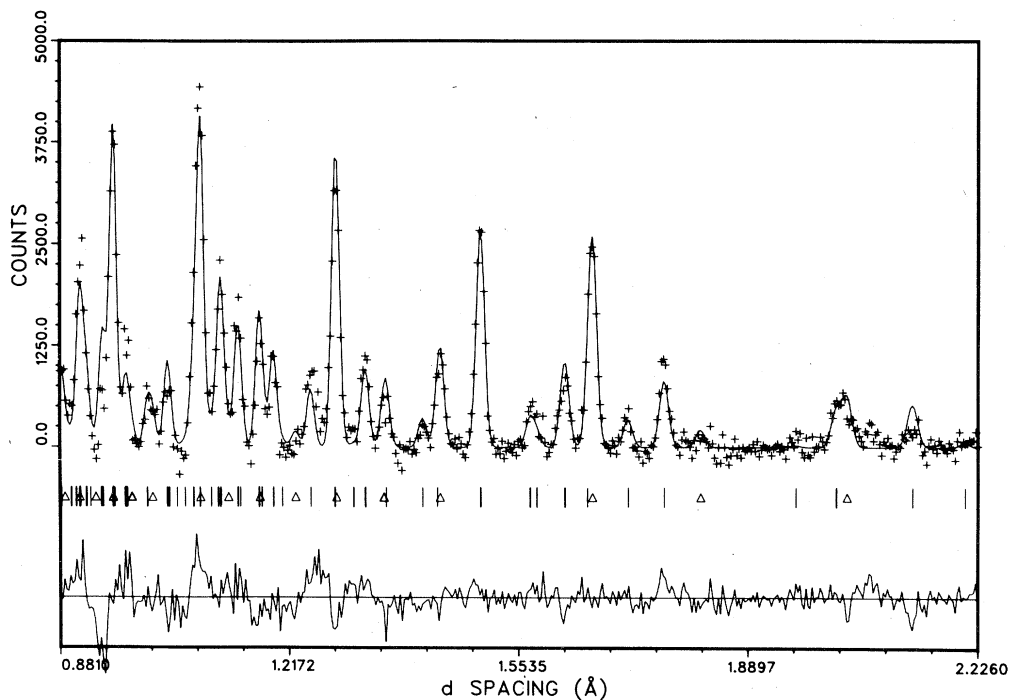


FIG. 2. Rietveld refinement profile for InBi and CsCl at 7.3 kbars. Plus marks (+) are the raw data. The solid line is the best-fit calculated profile. Background has been subtracted before plotting. Tick marks (|) below the profile indicate the positions of all allowed InBi reflections. Similarly, triangles (Δ) indicate positions of allowed CsCl reflections. A difference plot appears at the bottom.

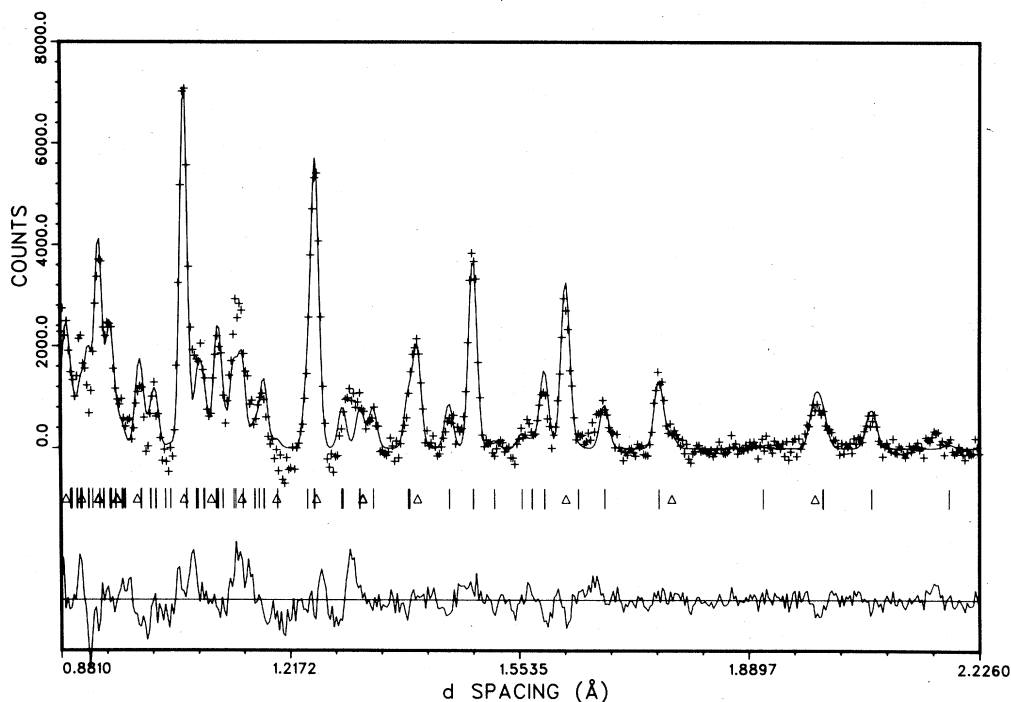


FIG. 3. Rietveld refinement profile for InBi at 25.6 kbars. Format is the same as Fig. 2.

ables in the minimization. A typical diffraction profile included 69 independent InBi reflections and 20 CsCl reflections in 450 time-of-flight data points extending from $d = 0.86$ – 2.36 Å. The refined CsCl lattice parameter was used to calculate the sample pressure based on Decker's equation of state.¹⁴

Raw data and calculated diffraction profiles at 7.3 and 25.6 kbars are shown in Figs. 2 and 3. Background has been subtracted before plotting, but it was unusually high, varying smoothly from about 4×10^4 counts per channel at $d = 0.88$ Å to about 1×10^4 counts per channel at $d = 2.23$ Å. This abnormally poor signal-to-noise ratio stems at least partially from the rather large neutron absorption cross section of In and was the main reason for the rather long (48 h) counting times. Nevertheless, the statistics are still not as good as one would like, as evidenced by the difference plots in Figs. 2 and 3.

RESULTS

The first obvious conclusion to be drawn from the diffraction data is that no first-order structural transition occurs up to 25.6 kbars. The data can be fit equally well with the $P4/nmm$ tetragonal space group for all of the high-pressure runs. Additionally, there is no evidence for any subtle

second-order strain transition which would result in line broadening. In particular, the width of the large 311 reflection at 1.49 Å remains in perfect agreement with the known instrumental resolution function up to the highest pressures studied, thus precluding any significant orthorhombic strain.

The measured lattice parameters, Bi atomic position parameter z , and temperature factors for InBi versus pressure are listed in Table I along with the nearest-neighbor Bi–Bi and In–Bi distances calculated from a , c , and z . The conventional unweighted Rietveld R value for these fits lies between 0.24 and 0.28 with the major problem in fitting being the unusually poor signal-to-noise ratio. (In fact, the R value calculated with background included is near 0.01 and reduced χ^2 is about 0.04). Difficulties in accurately fitting the background may also contribute to the rather large apparent pressure dependence of the temperature factors. Thus, the reported values for $B(\text{In})$ and $B(\text{Bi})$ should be considered somewhat suspect. Moreover, the poor signal-to-noise ratio and long counting times enhance the sensitivity to erroneous peaks from the surrounding pressure cell which may be present in the higher-pressure runs.

For the Rietveld technique, the refined lattice parameters are relatively insensitive to the poor

TABLE I. Lattice parameters, Bi atomic position parameter z , temperature factors, and Bi-Bi and In-Bi nearest-neighbor distances versus pressure for InBi. Numbers in parentheses are statistical uncertainties of last significant figure. Temperature factors are defined e^{-B/Ad^2} .

Pressure (kbar)	a (Å)	c (Å)	z	$B(\text{In})$ (Å ²)	$B(\text{Bi})$ (Å ²)	Bi-Bi (Å)	In-Bi (Å)
0.0	5.0118(8)	4.7790(14)	0.3924(13)	2.8(3)	1.3(2)	3.690(3)	3.130(4)
7.3(5)	4.9979(12)	4.7116(21)	0.3972(15)	1.6(3)	1.7(2)	3.664(4)	3.122(4)
13.9(5)	4.9901(10)	4.6527(17)	0.4038(16)	1.3(3)	1.6(3)	3.640(4)	3.123(4)
18.7(5)	4.9841(9)	4.6023(17)	0.4024(16)	0.8(3)	1.8(3)	3.637(4)	3.105(4)
25.6(5)	4.9732(11)	4.5524(18)	0.4054(18)	0.6(3)	2.7(3)	3.621(5)	3.097(5)

signal-to-noise ratio; however, atomic position parameters could be adversely affected. In an attempt to determine how these problems might affect the accurate determination of the Bi atomic position parameter z , the entire set of data was refined under two different constraints in addition to the unconstrained refinement reported. In one case, the temperature factors were held fixed at their atmospheric-pressure values. In the second case, regions where impurity peaks were suspected (based on large discrepancies in the difference plots) were ignored during the minimization. Both of these refinements gave nominally the same values for z as the unconstrained refinement reported. This is what might be expected, since z is the only variable position parameter in this simple structure and is therefore somewhat overdetermined. Moreover, the profile-refinement technique used to analyze these data¹³ fits the background along with the structural parameters rather than subtracting out the background before fitting, as is often done. Thus, correct weighting and statistics are preserved in the fitting procedure and, more importantly, contributions to the statistical uncertainties of structural parameters caused by the unusually high background are correctly handled in the error matrix.

The pressure dependence of the lattice parameters a and c is plotted in Fig. 4. The average compressibility along c from these data is about six times that observed along a . Within the experimental uncertainties, the observed pressure dependence of c is nearly linear; however, the pressure dependence of a appears to depart from linearity in a systematic way with the largest compression occurring at the lower pressures, a shallow minimum in the compressibility around 14 kbars, and increasing compression upon going from 14 to 25.6 kbars. This agrees qualitatively with the results of Fritz³ who reported that the compressibility along a exhibits a broad minimum equal to about $\frac{1}{3}$ of its initial value occurring around 15 kbars, while the compression along c

decreased only about 20% at high pressure. Since the change in unit-cell volume is dominated by the large compressibility along c , which is nearly linear, the volume compressibility shows only a small, smooth departure from linearity, as illustrated in Fig. 5. Thus, it is no surprise that Gordon and Deaton⁶ did not observe any anomalies in their high-pressure volumetric studies of InBi.

A quantitative comparison with the results of Fritz is difficult with these limited data. However, these results seem to differ from those of Fritz in at least three ways. First, the diffraction data indicate that the average compression along c is about six times that along a , while Fritz reported an order-of-magnitude difference. Second, the minimum in compression along a is not as pronounced as observed by Fritz. Third, the small (20% at 24 kbars) decrease in compression along c versus pressure reported by Fritz is not

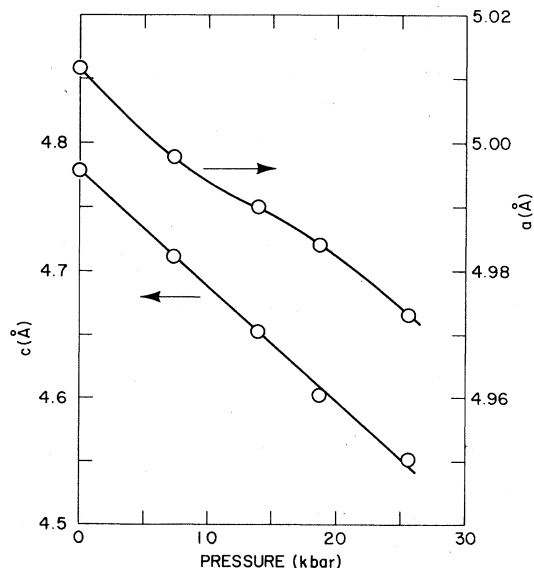


FIG. 4. Tetragonal lattice parameters a and c for InBi versus pressure. Solid lines are simply guides to the eye. Uncertainties are smaller than the points.

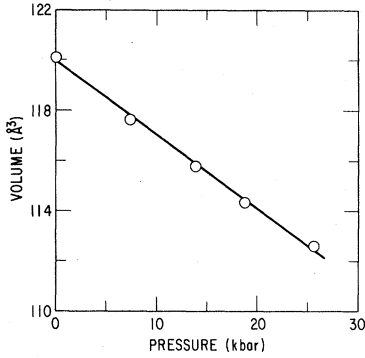


FIG. 5. Unit-cell volume for InBi versus pressure. The straight line through the data shows the small departure from linear behavior. Uncertainties are smaller than the points.

observed in the diffraction data. These differences could result from a less hydrostatic environment for the diffraction measurements. The technique used for this work involves first filling the Teflon sample container with the powdered sample (not tightly packed) and then adding the Fluorinert FC-75 liquid to fill the voids between particles. Thus, even though Fluorinert remains liquid to at least 20 kbars¹⁵ and is quite hydrostatic to about 30 kbars (as evidenced by lack of broadening of CsCl lines), there is the possibility of some nonhydrostatic forces resulting from direct contact between powder particles.

The Bi-Bi and In-Bi nearest-neighbor distances show the interesting pressure dependence plotted in Fig. 6. Based on the five pressures for which data were taken, the nearest-neighbor distances seem to show a distinct break in their pressure dependence near the points at 13.9 kbars. The

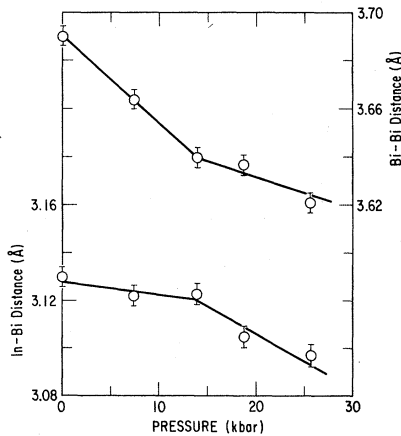


FIG. 6. Bi-Bi and In-Bi nearest-neighbor distances in InBi versus pressure. Straight lines through the data above and below 13.9 kbars emphasize the apparent changes in slopes at this pressure.

Bi-Bi distance decreases more rapidly below this pressure than above, while the In-Bi distance shows the opposite behavior. The straight lines through the data with different slopes above and below 13.9 kbars serve only to emphasize the changes in slope which appear to occur. Obviously, with the limited number of data reported here it is difficult to specify the pressure at which the anomaly in nearest-neighbor interactions occurs or to ascertain whether the change is gradual or well localized.

DISCUSSION

The results reported in this study show that even though no ordinary structural phase transitions occur in InBi below 25 kbars, some interesting anomalous behavior does occur in the pressure dependence of the compressibility in the plane perpendicular to c and in the pressure dependence of Bi-Bi and In-Bi distances. The best explanation for this anomalous high-pressure behavior is the proposal by Schirber and Van Dyke⁸ that a Lifshitz⁹ electron transition occurs as a small hole pocket disappears upon increasing pressure.

In the original paper by Lifshitz,⁹ and also in more recent treatments of the Lifshitz transition,¹⁶ the expected compressibility anomaly has been discussed only for the case of an electron pocket appearing upon increasing pressure. The effect of a hole pocket can be derived following the method of Lifshitz.⁹ The critical bands in the region of the Van Hove singularity at $E = E_c$ can be described by⁹

$$E(p) = E_c - \frac{p_1^2}{2m_1} - \frac{p_2^2}{2m_2} - \frac{p_3^2}{2m_3}, \quad (1)$$

and the corresponding Van Hove anomaly in the electron density of states is

$$\delta n(E) = \begin{cases} \alpha(E_c - E)^{1/2}, & \alpha \sim N/E_F^{3/2}, \quad E_c > E \\ 0, & E_c < E \end{cases}$$

where E_F is the Fermi energy and N is the total number of states. The resulting contribution to the free energy (as $T \rightarrow 0$) is

$$\delta F(E_c - E_F) = \begin{cases} -\frac{4}{15} \alpha (E_c - E_F)^{5/2}, & E_c > E_F \\ 0, & E_c < E_F \end{cases}$$

Denoting by V_c the volume at which $E = E_c$ and taking $(E_c - E_F) = \gamma(V_c - V)$, where V is the volume, the anomaly in $\partial P / \partial V$, where P is pressure, associated with the electron transition is

$$\delta \frac{\partial P}{\partial V} = -\delta \frac{\partial^2 F}{\partial V^2} = \begin{cases} \alpha \gamma^2 (E_c - E_F)^{1/2}, & E_c > E_F \\ 0, & E_c < E_F \end{cases}$$

Thus, for a hole pocket, in the region of the electron transition the negative quantity $\partial P/\partial V$ obtains a positive increment $\sim(E_c - E_F)^{1/2}$ for $E_c > E_F$. This is in contrast to the case for an electron pocket, where $\partial P/\partial V$ obtains a positive increment $\sim(E_F - E_c)^{1/2}$ for $E_F > E_c$.

The compressibility data from this work and that of Fritz³ are in good qualitative agreement with the theory. Based on the extrapolation of Schirber and Van Dyke's dHvA data, the hole pocket corresponding to the α frequency disappears at 12.6 kbars at low temperature.⁸ At room temperature the transition would be expected to occur at a slightly higher pressure and, in addition, would be thermally smeared. Below the pressure of the electron transition (i.e., for $E_c > E_F$), a sharp rise in compressibility along a ($\partial a/\partial P$) is observed both in this work and in that of Fritz.³ The best quantitative measure of compressibility versus pressure comes from the work of Fritz, which shows that $\partial a/\partial P$ is roughly three times larger at atmospheric pressure than at 15 kbars.

The absence of a well-defined anomaly in the compression along c could indicate that $(E_c - E_F)$ for the hole pocket depends much more strongly on a than on c . Further evidence for this is seen in the pressure dependence of In-Bi and Bi-Bi distances, where the most dramatic change is observed in the Bi-Bi distances which lie predominantly in the plane of the corrugated Bi layers. However, since the compression along c is an order of magnitude larger than along a , due to the anisotropy of the layered structure, a small positive increment in $\partial P/\partial c$, equal in magnitude to the one observed in $\partial P/\partial a$, would be difficult to detect. The band calculations of Schirber and Van Dyke show that the occurrence of the Lifshitz transition results from the pronounced pressure

dependence of c/a , which brings about a relative motion of bands.⁸ They did not investigate the relative importance of structural changes within the layers versus changes normal to the layers.

The transition pressure reported in this work is in good agreement with the elastic measurements of Fritz³ and the dHvA results of Schirber and Van Dyke (considering the effect of temperature).⁸ Conversely, the sharp resistance anomaly reported by Rapoport *et al.* was at 19 kbars.⁴ One possible explanation for this difference could be sample composition. The Fermi level, and thus the pressure of the electron transition, would be quite sensitive to impurity concentration and more importantly to stoichiometry of the InBi sample. A more probable explanation is that significant changes in the transition pressure could result from nonhydrostatic conditions in the pressure cell. The smaller anisotropy reported here, as compared to Fritz's result for elastic measurements on a single-crystal sample, may indicate that the pressure behavior of InBi is very sensitive to nonhydrostatic stresses. Assuming that the smaller pressure dependence of c/a observed in this study results from slightly nonhydrostatic conditions, it is not unlikely that the higher transition pressure of 19 kbars reported by Rapoport *et al.* results from the nonhydrostatic sample environment for their samples. They observed the resistance anomaly at 19 kbars only for samples embedded in epoxy and studied in a Bridgman opposed-anvil apparatus.

ACKNOWLEDGMENTS

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