PHYSICAL REVIEW B, VOLUME 65, 140101(R)

Evidence of a Lifshitz transition in the high-pressure behavior of the intermetallic compound $AuIn_2$

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(Received 14 February 2002; published 4 April 2002)

Accurate equation of state of $AuIn_2$ was obtained by x-ray diffraction measurements with ELETTRA synchrotron source to pressures over 20 GPa. Below 5 GPa, the P-V data when transformed to universal equation of state (UEOS), shows a deviation from linearity, confirming an electronic transition, consistent with the anomaly observed earlier in fusion and electrical data. The present high-resolution data also reaffirm a structural phase transition beyond 9 GPa. Full potential electronic band-structure calculations reveal a Lifshitz transition at the observed anomaly in the UEOS. Its transition pressure was found to be sensitive to the exchange-correlation terms.

DOI: 10.1103/PhysRevB.65.140101 PACS number(s): 62.50.+p, 61.66.Fn, 64.70.Kb, 82.40.Fp

Predictions of phase transitions at high pressures and their confirmations using diamond anvil cell measurements have led to significant improvements in density-functional theories for exchange-correlation potentials beyond the local-density approximation (LDA).[1] The emphasis so far has been to generate simultaneously pressures of several megabars and temperatures of several thousands of degrees Kelvin to obtain physical conditions in the laboratory that mimic those existing in the mantle and core of the earth, in order to enable studies on its constituent materials.[2] However, the moderate pressure region continues to remain exciting with the observations of certain phenomena and associated controversies in the data.[3,4] One of the most dramatic manifestations of subtle electronic structure changes brought about by pressure has been the exhibition of anomalies in the thermodynamic properties of materials. Some of these anomalies occur due to the proximity of an energy band extremum (Van Hove singularity) to the Fermi level (E_F), and its passage through E_F as the pressure is varied, known as Lifshitz transitions or electronic topological transition (ETT).[5,6] There had been difficulties till the recent past in correlating them with experimental data due to the lack of controlled high-pressure experiments and precision in the pressure volume (P-V) measurements.[7] The availability of synchrotron sources and incorporation of an imaging plate area detector in the angle dispersive x-ray diffraction (ADXRD) technique have made it possible.[2] In the present work, we demonstrate an interesting interplay between state-of-the-art results of first-principles calculations and experimental data yielding evidence of a Lifshitz transition for an intermetallic, $AuIn_2$.

The significance of present investigations is in providing a method to identify an ETT. The traditional methods used for its detection in transport properties and superconducting transition temperature (T_c) measurements are indirect, like when no other significant change is known to occur, the observed anomaly is attributed to an ETT. In the present work, we identify its presence experimentally from the equation of state measurements, which can be calculated from theory with more ease compared to T_c and thermoelectric power (TEP). This has been possible with the availability of intense synchrotron source that enables accurate measurements of diffraction data at small intervals of pressures. The compound $AuIn_2$ crystallizing in the calcium flourite (CaF_2) structure,[8] exhibits anomalies in various physical properties, such as variation with pressure of fusion temperature, TEP, and electronic and structural behaviors. Hence it serves as an excellent prototype to demonstrate the interesting interplay between theory and experiment for high-pressure investigation. Also, as several oxides of geophysical interest occur in CaF_2 structure, phase transformation studies under compression on intermetallic compounds in this structure are useful in providing information concerning the high-pressure metallic phases of these oxides. Whereas most of the current electronic structure calculations related to geophysical materials are being carried out at 0 K, the finite temperature effects have been included in the present work. It is possible to extend these to higher temperatures, a case in which the temperature corrections, such as the entropy effects would be more significant. These temperature effects are important since most of the phenomena of geophysical interest exist at high temperatures. For example, another structure was observed in iron in the pressure range 44–100 GPa between 2100 and 2300 K, whereas the related electronic structure calculations were carried out at 0 K.[2,4] Also, most of the studies related to geophysical materials focus on structural transitions only, and the electronic transitions, like ETT, are usually not investigated. The present work highlights the fact that such transitions could also be equally important leading to anomalies in physical properties, and can be relevant to geophysical modeling. Further the applicability of the present method to detect ETT is not limited to $AuIn_2$ but is quite general. With the availability of very high pressure to which variety of materials can be subjected, it will be possible to detect ETT in them.

Storm *et al.*[9] studied the fusion behavior of the intermetallic compound $AuIn_2$ up to a pressure of 5 GPa, and found

that its fusion curve remains nearly constant up to about 3 GPa, beyond which it acquires a positive slope. Godwal *et al.*[10] carried out high-pressure electrical resistivity, TEP, and x-ray diffraction measurements to investigate this anomaly. While the rotating anode generator based high-pressure ADXRD data indicated a structural phase transition beyond 8 GPa, TEP measurements showed a peak in the 2–4 GPa pressure range. The detailed band structure under pressure obtained by linearized muffin-tin orbital (LMTO) calculations within the atomic sphere approximation (ASA)[11] revealed that this transition is due to an ETT. The theoretical universal equation of state (UEOS)[7,12] obtained from the calculated P-V curve showed deviation from linearity in this pressure range. However, the lack of precise data at close intervals of pressure prevented its verification. In its absence, the theoretical conjecture that ETT[5] is the cause of anomaly in UEOS[7] and high-pressure fusion[9] and electrical[10] data is questionable in view of the inherent accuracy limitations of atomic sphere approximation.[11] The present experimental and theoretical studies are aimed at improving upon those limitations by carrying out high-pressure ADXRD measurements using a synchrotron source, and by carrying out temperature-dependent electronic band-structure calculations using the full potential linearized augmented plane-wave (FP-LAPW) method.[13]

High-pressure x-ray diffraction measurements were carried out using the synchrotron radiation source at ELETTRA, Trieste, Italy. Clamp-type Merrill-Bassett and Mao-Bell diamond anvil cells fabricated by us were employed.[14] Fine particles of $AuIn_2$ were loaded into a hardened stainless-steel gasket hole of 150 μm diameter along with silver as an internal pressure marker. Ethanol was used as the pressure transmitting medium. The ELETTRA diffraction beam line is designed to provide a monochromatized, high-flux, tunable x-ray source in the spectral range between 4 and 25 KeV.[15] The experimental station is based on a 345-mm imaging plate area detector from MarResearch. The sample to imaging plate distance was calibrated by collecting diffraction data from silver loaded in the diamond anvil cell. The x-ray wavelength used was 0.690 Å.[15] The data were collected up to 20 GPa with a typical exposure time of 15 min at each pressure. The scanned two-dimensional diffraction patterns were corrected for tilt and scanner distortions and converted to intensity versus 2θ through radial integration using our own[16] and public-domain softwares.[17] The precision in the d values obtained using ELETTRA synchrotron was higher by almost a factor of two compared to that obtained with laboratory x-ray source (rotating anode generator).

The evolution of diffraction patterns at various pressures is shown in Fig. 1. Below 9 GPa the patterns could be indexed to the ambient cubic (space group $Fm3m$) phase. These patterns reveal that $AuIn_2$ transforms to another phase above 9 GPa, as confirmed by the variation of the measured d values with pressure (not shown), in agreement with earlier observations.[10] Having confirmed that structural change is not responsible for the observed anomaly in the fusion curve, and based on our observation of a peak in the pressure variation of TEP data,[10] we anticipated some significant change in

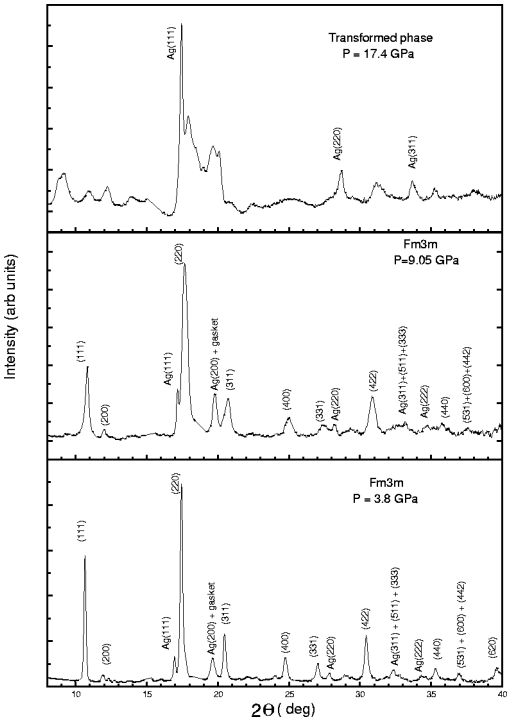

FIG. 1. Evolution of diffraction patterns at various pressures for $AuIn_2$.

the electronic structure of $AuIn_2$ under pressure. In particular, electronic transitions will lead to deviation from linearity in the UEOS.[7] Hence, we obtained an accurate P-V curve (Fig. 2) from the measured d values and analyzed it through the use of UEOS, in order to look for signature of the electronic anomaly suggested earlier.[10] As observed from Fig. 3 there indeed is a change of slope at 3.8 GPa.

In order to confirm that ETT is the cause of the anomaly seen in UEOS and to improve upon the accuracy limitations of earlier ASA[11] based calculations, we carried out accurate

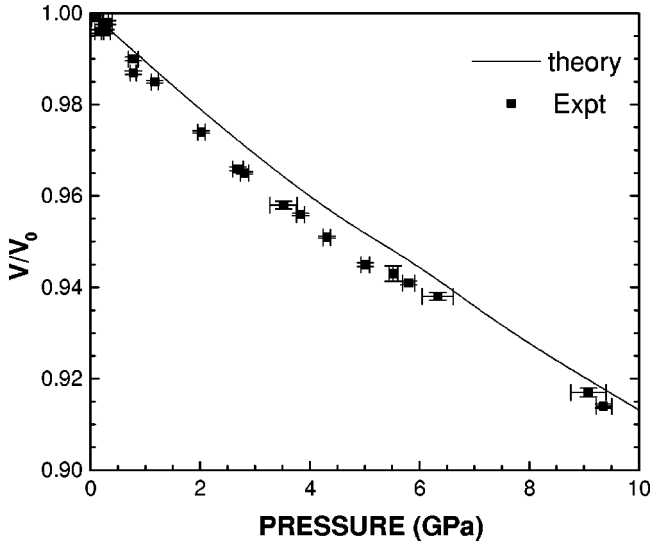

FIG. 2. Equation of state for $AuIn_2$. The experimental data points are shown along with the error bars in V/V_o and pressure.

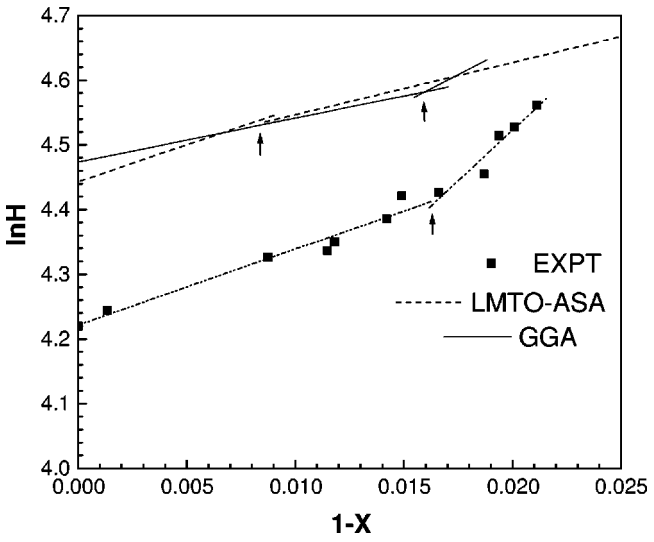

FIG. 3. Universal equation of state [i.e., ln$H$ versus $(1-X)$] for $AuIn_2$, where $H=[PX^2/3(1-X)]$ and $X=(V/V_o)^{1/3}$. The curves include the bulk moduli evaluated at ambient pressure. The arrows indicate the electronic transition points.

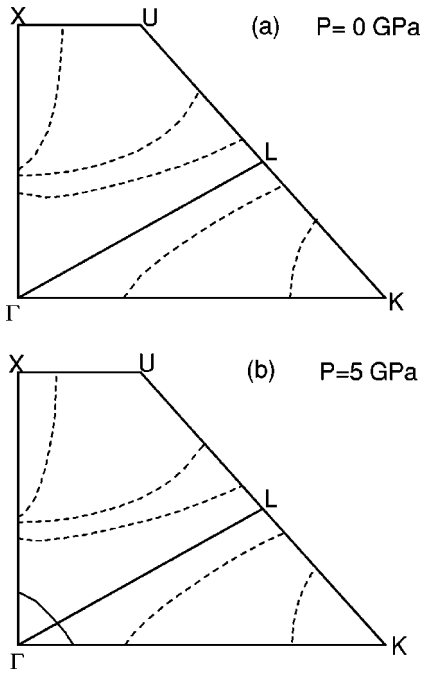

FIG. 4. Fermi-surface sheets (a) at ambient pressure, and (b) at 5 GPa. The hole sheet around Γ point arising due to ETT is shown by a solid curve. The Fermi-surface sheets of the other bands are shown by the dashed curves.

electronic structure calculations in the CaF_2 structure for $AuIn_2$ by the FP-LAPW method.[13] We have used the WIEN97 code[13] with a state-of-the-art generalized gradient approximation (GGA)[1] for the exchange-correlation terms. The calculations were also repeated within the LDA[18] to estimate the sensitivity of the results of exchange correlation. We employed the symmetrized cubic harmonics inside the muffin-tin spheres and 243 plane waves in the interstitial region for wave function expansion. We applied the spin-orbit correction terms and used 5000 **k** points for the Brillouin-zone sampling. As the experiments were performed at room temperature, the electronic structure calculations were carried out at 300 K based upon nonzero temperature density-functional theory.[19] The set of self-consistent Kohn-Sham equations to obtain the ground-state electronic charge density distribution are similar to those in the 0-K case, and the main modification is in evaluating the charge density with the Fermi function corresponding to nonzero temperature. We accordingly modified the tetrahedron method of Brillouin-zone integration in evaluating the electron-density distribution. The details of these modifications are published elsewhere.[20] As the free-energy minimization is central to the finite temperature density-functional theory, the necessary entropy contribution due to nonintegral values of electron distribution function at room temperature were also estimated. However, for $AuIn_2$ at 300 K, this entropy contribution is small compared to the needed accuracy in evaluating the total internal energy, but will be significant at higher temperatures. The total energies were obtained at several volumes in CaF_2 structure, fitted to a polynomial, and the corresponding pressures were evaluated from its volume derivatives.

In Fig. 2 we compare the EOS in which contributions from zero-point and thermal ionic vibrations have been included[21] with that obtained from our experimental data. The marginal discrepancy between theory and experiment may partly be attributed to the limitations of the exchange-correlation terms as noted earlier.[10,22,23] The transformation of theoretical P-V data to UEOS, following Rose *et al.*,[7] shows similar features as depicted by the experimental data with an anomaly around 3.6 GPa (Fig. 3). In Fig. 3 we have also plotted the LMTO-ASA based UEOS, which clearly indicates the deviation from linearity near 2 GPa. As the discrepancies are known to get magnified in the transformed coordinates of the UEOS (due to relative expansion of the scale in the low-pressure region in the logarithmic scale), as compared to the P-V curve, within the experimental precision and accuracy of the current first-principles calculations, the qualitative agreement between the high-resolution synchrotron data and the theoretical estimate of the transition pressure is remarkable.

From detailed study of our band structure, we found that a band extremum (maximum) at the Γ point of the Brillouin zone, exists close to Fermi level (E_F) and is lower in energy at ambient pressure. With compression this extremum moves to higher energies, and for the LDA case, it crosses E_F at around 0.6 GPa pressure, whereas for GGA at around 3.6 GPa. Figure 4 shows the corresponding changes in Fermi-surface sheets before and after the ETT, and depicts the additional hole sheet around the Γ point at 5 GPa, this being the cause of the nonlinearity in UEOS. The theoretical estimate of the transition pressure for ETT has been found to be very sensitive to the form of the exchange-correlation term used. However, the present GGA based pressure estimate for the anomaly in the UEOS is close to that obtained by using the experimental data. The fact that the anomaly in UEOS has been relatively well reproduced by the theoretical estimates, whereas the band crossing for ETT is not, indicates the need for further refinements in the calculations. Note that

the UEOS depends on the total energy, which is accurately estimated by density-functional theory, whereas the electron excitation band structure is not. Thus it is interesting to see the estimates of calculations beyond the density-functional theory, like the Green's-function-screened Coulomb[24] quasiparticle computations. Although the present work deals with condensed-matter regime, its applicability is expected to go beyond this subfield boundary to nuclear matter where similar universal scaling relations are used.[25]

The measurements were carried out at ELETTRA under Proposal No. 1999126 and supported jointly by Sincrotrone, Trieste, Italy and DST, India.

[1] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[2] D. Andrault *et al.*, Science **278**, 831 (1997).

[3] B. Palanivel, R.S. Rao, B.K. Godwal, and S.K. Sikka, J. Phys.: Condens. Matter **12**, 8831 (2000).

[4] R.S. Rao, P. Modak, B.K. Godwal, and S.K. Sikka, Phys. Rev. B **59**, 13 498 (1999).

[5] I.M. Lifshitz, Zh. Eksp. Teor. Fiz. **38**, 1569 (1960) [Sov. Phys. JETP **11**, 1130 (1960)].

[6] L. Dagens, J. Phys. F: Met. Phys. **8**, 2093 (1978).

[7] For example, for demonstrating the deviation of the universal equation of state from linearity as a result of such electronic transitions. [see P. Vinet *et al.*, J. Geophys. Res. **92**, 9319 (1987); J.M. Rose *et al.*, Phys. Rev. B **29**, 2963 (1984); S.K. Sikka, Phys. Rev. B **38**, 8463 (1988)].

[8] C. Barrett and T.B. Massalski, *Structure of Metals*, McGraw-Hill Series in Material Science and Engineering (Eurasia, New Delhi, 1966).

[9] A.R. Storm, J.H. Wernick, and A. Jayaraman, J. Phys. Chem. Solids **27**, 1227 (1966).

[10] B.K. Godwal, A. Jayaraman, S. Meenakshi, R.S. Rao, S.K. Sikka, and V. Vijayakumar, Phys. Rev. B **57**, 773 (1998).

[11] O.K. Andersen, Phys. Rev. B **12**, 3060 (1973).

[12] The *P*-*V* data was transformed to universal equation of state with details discussed in Ref. 10.

[13] P. Blaha *et al.*, Phys. Rev. B **37**, 2792 (1988); P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology 1997 [improved and updated UNIX version of the original copyrighted WIEN code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, Comput. Phys. Commun. **59**, 399 (1990)].

[14] V. Vijayakumar and S. Meenakshi, BARC Report No. BARC/2000/1/014 (unpublished).

[15] E. Bussetto, A. Lausi, and A. Paverse, in *Sincrotrone Trieste, Seventh Users Meeting* (ICTP, Trieste, Italy, 1999), p. 29.

[16] The diffraction patterns obtained by using the software developed by V. Vijayakumar, Alka B. Garg, and Amar Sinha (unpublished) were compared with those calculated using commercially available FIT2D software (Ref. 17).

[17] A.P. Hammersley *et al.*, High Press. Res. **14**, 235 (1996).

[18] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[19] W. Kohn and P. Vashishta, in *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundquist and N.H. March (Plenum Press, NY, 1983) p. 79; N.D. Mermin, Phys. Rev. **A137**, 1441 (1965).

[20] B.K. Godwal, P. Modak, and R.S. Rao (unpublished).

[21] B.K. Godwal and R. Jeanloz, Phys. Rev. B **41**, 7440 (1990).

[22] The calculated equilibrium volume using GGA (Ref. 1) is about 10% higher compared to the experimental value (Ref. 10). These findings are contrary to the general understanding that GGA adequately describes the exchange correlation effects, and hence further improvements to it may be required (Ref. 23).

[23] J.P. Perdew *et al.*, Phys. Rev. Lett. **82**, 2544 (1999).

[24] W.E. Picket and C.S. Wang, Phys. Rev. B **30**, 4719 (1984); M.S. Hybertsen and S.G. Louie, *ibid.* **34**, 5390 (1986); R.W. Godby, M. Schulter, and L.J. Sham, *ibid.* **36**, 6497 (1987).

[25] J.H. Rose, J.P. Vary, and J.R. Smith, Phys. Rev. Lett. **53**, 344 (1984).