Two-dimensional pressure-induced electronic topological transition in Bi$_2$Te$_3$

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A structural peculiarity of the electronic topological transition (ETT) occurring within the pressure stability range of the low-pressure rhombohedral phase I has been evidenced in Bi$_2$Te$_3$. On both sides of the ETT the structure remains unchanged. Nevertheless, precise investigation of x-ray diffraction patterns allows us to conclude that this ETT obeys the lamellar character of this compound but in a counterintuitive way. Indeed, the signature of this ETT can be detected only in the layers' plane in the pressure variation of the lattice parameter *a* with a 25% increase of the lattice modulus and a 68% decrease of its pressure derivative. On the contrary, no singularity occurs perpendicularly to the layers of the Bi$_2$Te$_3$ structure.

I. INTRODUCTION

The size and shape of the Fermi surface may be tuned with external parameters such as the pressure (hydrostatic or uniaxial), composition, temperature, or magnetic field. Depending on the analytical shape of a critical energy E_c, a void can be formed or destroyed, or the neck connecting two parts of the Fermi surface may be disrupted. This can result in a modification of the topology of the Fermi surface. Such an electronic topological transition (ETT) or Lifshitz transition has been proposed and discussed by Lifshitz[1] at 0 K in the absence of impurity. He characterized it as a 2.5 transition in the Ehrenfest description of the phase transitions. No discontinuity of the volume is then expected in the vicinity of the transition (first derivative of the Gibbs free energy), but a variation of the second derivative of the Gibbs free energy, i.e., of the compressibility, is expected. This transition may also be detected by phonon softening. Actually the transport properties are also expected to probe the ETT[2] because the transition involves the Fermi surface.

In fact this type of transition has been shown to greatly influence the thermoelectrical properties of compounds.[3,4] Then the interest of the ETT is not only theoretical, and such a transition and consequently thermoelectrical properties can be expected to be easily monitored in low-dimensional compounds in which a competition between ionocovalent bonds within the layers and weak van der Waals forces between layers plays a central role.

From this point of view, Bi$_2$Te$_3$ is an extremely peculiar and promising compound belonging to the family of the V$_2$-VI$_3$ compounds with singular and very interesting properties. For example, it has been claimed to be a topological insulator,[5–7] i.e., "a new state of quantum matter that is characterized by a finite energy gap in the bulk and gapless modes flowing along the boundaries that are robust against disorder scattering."[8]

It is to date one of the best thermoelectrical compounds,[9–11] whose figure of merit presents its maximum value around the ambient temperature.[12] The pressure has a large positive effect on the thermoelectric power of the compounds of this family, such as Sb$_{1.5}$Bi$_{0.5}$Te$_3$,[13] which has even been qualified as giant improvement in the case of Bi$_2$Te$_3$.[10] It has also been shown[11] that there is a large difference in the energy gap pressure coefficient related to the presence of the ETT, its value being −20 meV/GPa below and −60 meV/GPa above the ETT.

Previously published structural results on Bi$_2$Te$_3$ are controversial. Jacobsen *et al.*[14] proposed the existence of an electronic topological transition around 3 GPa from a very faint kink on the volume variation under pressure. The initial bulk modulus and its pressure derivative are $B_0 = 56.2$ GPa and $B' = 2.1$. Later, Nakayama *et al.*[15] reported a two domain behavior with a volume jump in the stability range of phase I. The parameters are $B_0 = 21.85 \pm 0.2$ GPa with $B' = 17.13 \pm 0.49$ below 1.5 GPa, and $B_0 = 38.19 \pm 0.42$ GPa with $B' = 4.61 \pm 0.16$ above 2 GPa. To explain this anomalous behavior the authors invoke that "... the electrical interactions between adjacent atoms change with the decrease of interatomic distances." At the same pressure, there is a minimum of the c/a lattice parameters ratio as a function of pressure. This property supports the presence of the anomaly of electron states at that pressure.[15] Hence there is no agreement on the transition pressure, and the values of the bulk modulus and its pressure derivative are very different. Moreover, there is no precise description of the transformation that occurs in the stability range of phase I.

In this Brief Report we present results of x-ray diffraction (XRD) as a function of pressure below the lowest first-order phase transition using a procedure used for Cd$_{0.8}$Hg$_{0.2}$.[16] We confirm the existence of the ETT. Moreover, an unexpected and

peculiar result of a careful analysis of the present data is that the modification of the Fermi surface topology is a structurally related effect with modifications in the layer planes only.

II. EXPERIMENTAL

We have produced the nanostructured Bi_2Te_3 compound by the mechanical alloying (MA) technique, a very efficient technique to synthesize many unique materials, such as nanostructured and amorphous alloys as well as metastable solid solutions.[17] One binary Bi-Te mixture of high-purity elemental powders of Bi (Aldrich 99.999%) and Te (Alfa Aesar 99.999%, −100 meshes) in the proportion 2:3 atomic was sealed together with several steel balls of 11.0 mm in diameter into a cylindrical steel vial under argon atmosphere. The ball-to-powder weight ratio was 7:1. The vial was mounted on a SPEX mixer/mill, model 8000. The temperature was kept close to the ambient temperature by a ventilation system. After 3 hours of milling, the measured XRD pattern was indexed to the rhombohedral Bi_2Te_3 phase, and the milling process was ended.

Membrane diamond anvil cell (DAC)[18] with an opening that allowed probing up to 28° of 2θ was used. The sample was prepared by compacting a small amount of Bi_2Te_3 powder between diamonds, to a final thickness of ∼15 μm. A small chip of this preparation, about 80 μm in diameter, was then loaded into a stainless-steel gasket hole of 150 μm diameter. A 4:1 methanol-ethanol mixture was used as a pressure-transmitting medium. The pressure was determined through the fluorescence shift of a ruby sphere[19] loaded in the sample chamber. The quasihydrostatic conditions were maintained throughout the experiments by monitoring the separation and widths of both $R1$ and $R2$ lines. We have performed x-ray diffraction measurements up to 31 GPa, and the results will be published elsewhere.[20] In this Brief Report we focus on the 0–9 GPa pressure range where the ethanol-methanol mixture is strictly hydrostatic.

In situ XRD patterns as a function of pressure were acquired at the XRD1 station of the ELETTRA synchrotron radiation facility. This diffraction beamline is designed to provide a monochromatized, high-flux, tunable x-ray beam in the spectral range between 4 and 25 keV.[21] The present experiment was performed using a wavelength of 0.6888 Å. The detector was a 345-mm imaging plate from MarResearch. The sample to detector distance was calibrated by diffraction data from Si powder standard loaded in the diamond anvil cell. The data were collected with a 10 min exposure time. The two-dimensional diffraction patterns were converted to intensity versus 2θ degrees using the fit2D software[22] and analyzed through the Rietveld method using the GSAS package.[23]

III. RESULTS AND DISCUSSION

Bi_2Te_3 is a layered compound, which at ambient conditions crystallizes in a rhombohedral structure $R\bar{3}m$ (S.G. 166, $Z = 3$) and its lattice parameters in the hexagonal setting are $a = 0.4383$ nm and $c = 3.038$ nm. One layer, i.e., one unit bonded through ionocovalent bonds, consists of five alternating sheets of Bi and Te. The succession is [Te(2)-Bi-Te(1)-Bi-Te(2)], where the Bi and the Te(2) atoms occupy the $6c$ Wyckoff sites
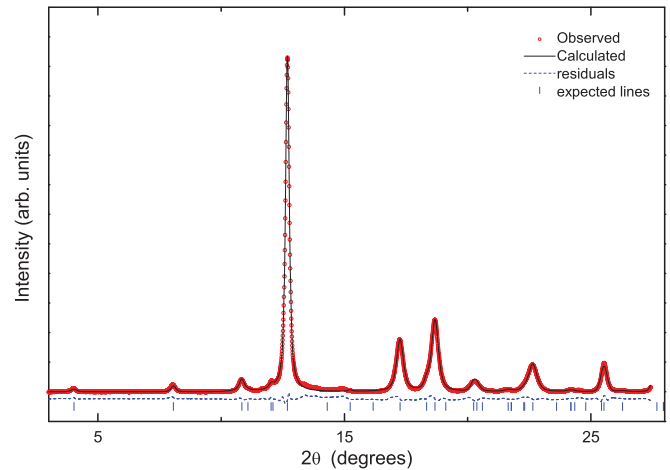

FIG. 1. (Color online) Rietveld fit to the x-ray pattern collected at 4.4 GPa at the XRD1 ELETTRA beamline.

(in the hexagonal setting) and the Te(1) atoms the $3a$ sites.[24] The hexagonal c axis is perpendicular to the plane of the layers, and the layers are bonded by van der Waals type bonds. The elementary piece of this structure is a $BiTe_6$ octahedron centered on a Bi atom. From this point of view layers are formed by two planes of adjacent edges sharing nonregular octahedra with common Te(1) atoms.

A typical diffraction spectrum is presented in Fig. 1, where the experiment is represented by the red dots, the refined spectrum by the continuous blue line, the difference between experiment and fit by the dashed line, and the expected diffraction lines by the vertical marks.

The lattice parameters $a(p)$, $c(p)$, the volume $v(p)$, as well as the inter- and intra-distances as a function of pressure are obtained from the Rietveld adjustments. Figure 2 shows a comparison of our results (full circles) with those of Jacobsen *et al.*[14] (open stars) and Nakayama *et al.*[15] (open squares). The continuous lines represent fits to a Birch-Murnaghan's equation of state (BM-EOS) expressed as

$$p = \tfrac{3}{2} B_0 X^5 (X^2 - 1) \left[1 + \tfrac{3}{4}(B' - 4)(X^2 - 1)\right] \quad (1a)$$
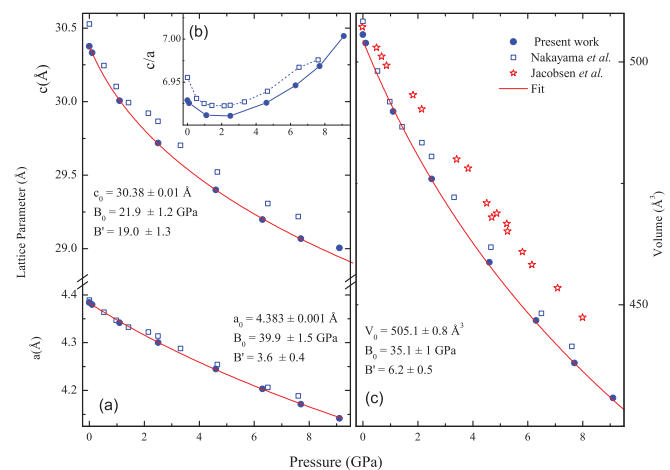

FIG. 2. (Color online) Pressure variation of the structural parameters of Bi_2Te_3 deduced from the Rietveld adjustments. (a) Lattice parameters; (b) c/a ratio; (c) volume.
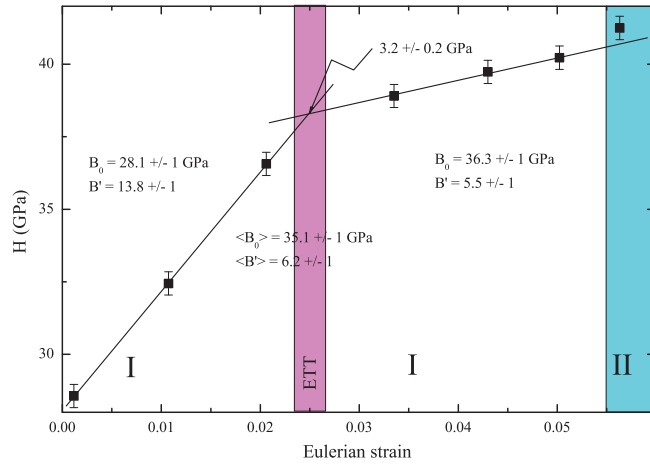
FIG. 3. (Color online) Electronic topological transition (ETT) found at 3.2 GPa. H defined in the text should be linear versus Eulerian strain for any stable compound. The linear regressions enable the determination of the bulk modulus and its pressure derivative (see text). Regions from both sides of the ETT transition have the same structure. The first shaded area represents the ETT pressure range and the second one the onset of the structural transition to phase II.[14,15,20]

with

$$X = \left(\frac{V_0}{V}\right)^{1/3}. \tag{1b}$$

A more accurate analysis of the experimental results can be done thanks to the BM-EOS linearization versus the Eulerian strain:

$$H = B_0 + \tfrac{3}{2} B_0 (B' - 4) f_E \tag{2a}$$

with

$$H = \frac{p}{3 f_E (1 + 2 f_E)^{5/2}} \tag{2b}$$

and

$$f_E = \tfrac{1}{2}(X^2 - 1). \tag{2c}$$

In the absence of any transition, H should be a linear function of f_E. $H(p = 0)$ is equal to the bulk modulus B_0 and its slope to its pressure derivative B'.

A plot the reduced pressure H [Eq. (2a)] as a function of Eulerian strains f_E is shown in Fig. 3. As already mentioned in Ref. 20, there is a clear kink around 3.2 GPa. One can observe that the values obtained here, $B_0 = 28.1 \pm 1$ GPa with $B' = 13.8 \pm 1$ below 3.2 GPa, and $B_0 = 36.3 \pm 1$ GPa with $B' = 5.5 \pm 1$, are in good agrement with those found by Nakayama et al.:[15] $B_0 = 21.85 \pm 0.2$ GPa ($B' = 17.13 \pm 0.49$) for pressures below 2 GPa and $B_0 = 38.19 \pm 0.42$ GPa ($B' = 4.61 \pm 0.16$) for pressures between 2 and 8 GPa. The 3.2 GPa pressure value for the change in the pressure dependence of the structural parameters is in good agrement with the proposed ETT pressure in Bi$_2$Te$_3$.[10]

It is possible to use the same procedure for the lattice parameter to check on which of the parameters the ETT plays the major role. In this case we have to replace Eq. (1a) either by $X_a = (a_0/a)$ or $X_c = (c_0/c)$. With these definitions for the X parameter, one defines H_a and H_c with the same analytical form as in Eq. (2) .

The results are shown in Fig. 4. It should be emphasized that the Eulerian strain abscissae are different for each lattice
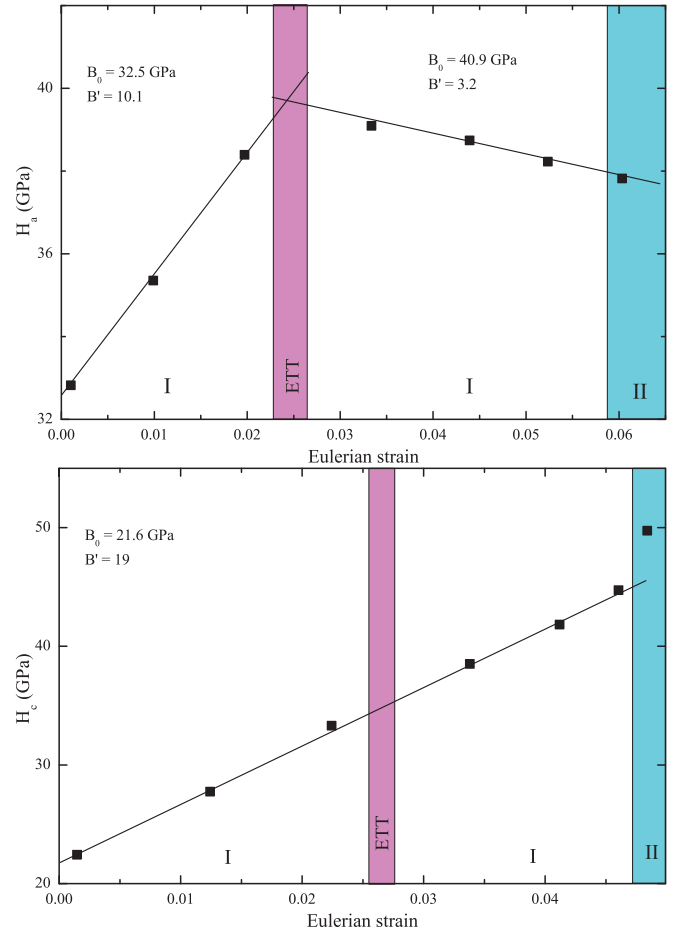

FIG. 4. (Color online) Reduced pressure plot versus Eulerian strain for the a and c lattice parameters. The electronic topological transition (ETT) is detected only on the pressure variation of the lattice a parameter (top) whereas the lattice c parameter is unaffected (bottom). The first shaded area represents the ETT pressure range and the second one the onset of the structural transition to phase II.[14,15,20]

parameter. Unexpectedly the pressure dependence of H_c is completely unaffected by the ETT (Fig. 4, bottom panel) in spite of the weakness of the interlayer interaction. On the contrary, H_a presents a very pronounced kink at 3.2 GPa (Fig. 4, top panel). Below the ETT the linear moduli B_a and B_c are respectively 32.5 and 21.6 GPa, and their pressure derivative B'_{0a} and B'_{0c} are large (respectively 10.1 and 19). Above the ETT, nothing changed for c but B_a increased to 40.9 GPa, and B'_a recovered the more "standard" value 3.2.

This transition is clearly different from a "standard" one. For example, in other layered compounds, such as GaS, an isogroup ($P6_3/mmc$) structural phase transition is observed at low pressure ($\sim$1.5 GPa)[25] where one layer shifts with respect to the other, resulting in a clear drop in the c axis, and hence in the volume. Here, the ETT is an isostructural transition but there is no volume variation at the transition and the Wyckoff positions of the atoms are not modified. Another important difference between the two types of transition arises from the clear two-dimensional character of the ETT. This is translated at the structural level by a sudden modification of the compressibility parallel to the layers' plane whereas the compressibility parallel to the c axis is constant although at that

pressure. It should be emphasized that the ethanol-methanol mixture is perfectly hydrostatic in this pressure range.

IV. CONCLUSION

In summary, the electronic topological transition has been confirmed in Bi_2Te_3 under pressure. Surprisingly the pressure dependence of the structural parameters related to weak van der Waals interactions seems to be insensitive to the modification of the Fermi surface. On the contrary the structural parameters related to the strong ionocovalent bonds are the only ones severely affected by the ETT with a 25% increase of the lattice modulus and a 68% decrease of its pressure derivative. The precise analysis of the diffraction pattern is hence very powerful and enables us to distinguish the effects of electronic transitions on the structures. This in turn may give hints in the search for the best compounds for thermoelectric applications.

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[1] I. M. Lifshitz, Sov. Phys. JETP (USSR) **11**, 1130 (1960).

[2] V. V. Struzhkin, Y. A. Timofeev, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **79**, 4262 (1997).

[3] E. S. Itskevich, L. M. Kashirskaya, and V. F. Kraïdenov, Semiconductors **31**, 276 (1997).

[4] N. V. Chandra Shekar, D. A. Polvani, J. F. Meng, and J. V. Badding, Physica B **358**, 14 (2005).

[5] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Phys. **5**, 438 (2009).

[6] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. L. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fischer, Z. Hussain, and Z. X. Chen, Science **325**, 178 (2009).

[7] L. Fu, Phys. Rev. Lett. **103**, 266801 (2009).

[8] Y. Zhang, K. He, C.-Z. Chang, C.-L. Song, L.-L. Wang, X. Chen, J.-F. Jia, Z. Fang, X. Dai, W.-Y. Shan, S.-Q. Shen, Q. Niu, X.-L.Qi, S.-C. Zhang, X.-C. Ma, and Q.-K. Xue, Nature Phys. **6**, 584 (2010).

[9] L. G. Khvostansev, A. I. Orlov, N. K. Abrikosov, T. E. Svechnikova, and S. N. Chizhevskaya, Phys. Status Solidi A **71**, 49 (1982).

[10] S. V. Ovsyannikov, V. V. Shchennikov, G. V. Vorontsov, A. Y. Maakov, A. L. Likhacheva, and V. A. Kulbachinskii, J. Appl. Phys. **104**, 053713 (2008).

[11] S. V. Ovsyannikov and V. V. Shchennikov, Chem. Mater. **22**, 635 (2010).

[12] T. M. Tritt, Science **283**, 804 (1999).

[13] D. A. Polvani, J. F. Meng, N. V. Chandra Shekar, J. Sharp, and J. V. Badding, Chem. Mater. **13**, 2068 (2001).

[14] M. K. Jacobsen, R. S. Kumar, A. L. Cornelius, S. V. Sinogeikin, and M. F. Nicol, AIP Conf. Proc. **955**, 171 (2007).

[15] A. Nakayama, M. Einaga, Y. Tanabe, S. Nakano, F. Ishikawa, and Y. Yamada, High Pressure Res. **29**, 245 (2009).

[16] B. K. Godwal, S. Speziale, S. M. Clark, J. Yan, and R. Jeanloz, J. Phys. Chem. Solids **71**, 1059 (2010).

[17] C. Suryanarayana, Prog. Mater. Sci. **46**, 1 (2001).

[18] J. C. Chervin, B. Canny, J. M. Besson, and P. Pruzan, Rev. Sci. Instrum. **66**, 2596 (1995).

[19] J. C. Chervin, B. Canny, and M. Mancinelli, High Pressure Res. **21**, 305 (2001).

[20] S. Michielon Souza, D. Menegon Trichês, J. Cardoso de Lima, T. Antonio Grandi, A. Polian, and M. Gauthier (unpublished).

[21] E. Bussetto, A. Lausi, and A. Paverse, *Proceedings of the Seventh Users Meeting*, ICTP, Trieste, Italy, 1999, p. 29.

[22] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Hausermann, High Pressure Res. **14**, 235 (1996).

[23] A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report LAUR 86-748 (2004).

[24] W. Kullmann, J. Geurts, W. Richter, N. Lehner, H. Rauh, U. Steigenberger, G. Eichhorn, and R. Geick, Phys. Status Solidi B **125**, 131 (1984).

[25] H. d'Amour, W. B. Holzapfel, A. Polian, and A. Chevy, Solid State Commun. **44**, 853 (1982).