High-pressure resistance and equation-of-state anomalies in Zn: a possible Lifshitz transition

High-pressure resistance and equation-of-state anomalies in Zn: a possible Lifshitz transition

Alka B Garg, V Vijayakumar, P Modak, D M Gaitonde, R S Rao, B K Godwal and S K Sikka

High Pressure Physics Division, Bhabha Atomic Research Centre, Mumbai-400 085, India

Abstract
Experimental results on electrical resistance variation with pressure up to 25 GPa are presented for zinc; they reveal the signature of an electronic topological transition. Theoretical estimates based on the results of first-principles band structure calculations corroborate the observed variation of the resistance. The Lifshitz transition, which is hardly observable in experimental P–V data, becomes discernible via the equation of state, in the universal as well as in Holzapfel's form. Another anomaly in the measured resistance is also observed around 20 GPa pressure. The resistance variation with pressure exhibits considerable hysteresis.

Elemental solid zinc crystallizes in the hexagonal close-packed (hcp) structure with a large axial ratio ($c/a = 1.856$) at ambient conditions. This makes its Fermi surface highly anisotropic, in spite of its wide s–p bands, resulting in anomalies in many of its properties [1–3]. A significant feature is the presence of a giant Kohn anomaly [4]. The application of pressure affects the bonding anisotropy and alters a variety of physical properties. This has led to intensive study of its high-pressure behaviour in the recent past, and it continues to puzzle theoretical and experimental groups [2, 3, 5–18] all over the world. The anisotropy of Zn reduces at high pressures as the axial ratio (c/a) reduces towards the ideal close-packing value of 1.633, and the deviation from a smooth decrease is known as its anomaly. Some of the most commonly discussed controversial areas relating to Zn are: the very existence of the high-pressure c/a anomaly; occurrence of the electronic topological transition (ETT) [19, 20] at the L point of the Brillouin zone (BZ); and the inter-relation between them [2, 3, 5, 6, 8–10, 12–14, 16, 18]. As is well known, the ETT, also known as the Lifshitz transition, relates to the passage of an extremum of the electron energy band (or equivalently of a van Hove peak in the density of states) through the Fermi level (ϵ_F).

The confusion about the c/a anomaly in Zn started with the direct x-ray diffraction (XRD) observation of strong and moderate [6, 21] anomalies, only attributable to the anisotropy or a phase transition in the pressure-transmitting medium [14]. The theoretical calculations also supported the occurrence of an anomaly (some of them predicting a strong one [9], but most of them showing a weak one [5, 13, 16]) near 10 GPa pressure. There were also suggestions that domains of different c/a should exist near 10 GPa, leading to c/a anomaly [12] and both L- and

K-point ETTs together contributing to it. It is now generally understood that the c/a anomaly is very weak, that it is probably difficult to detect under the currently attainable accuracies in the XRD data, and that the exaggerated anomalies obtained in the earlier calculations are mainly due to lack of accuracy in k-sampling of the BZ [17, 18, 40].

Regarding the ETT at the L point of the BZ, there are controversial reports of the observation of its signatures. The widespread interest in these measurements was initiated by the first-principles electronic structure calculations of Meenakshi *et al* [2], who obtained a weak c/a anomaly and attributed it to the shift of a van Hove peak in the density of states through the Fermi level (ϵ_F), i.e., to a Lifshitz transition. Subsequently Potzel *et al* [7] showed that an energy band minimum at the L point passed through the Fermi level at the pressure at which the Lamb–Mössbauer factor showed an anomalous drop, signalling the softening of low-frequency acoustic or optical phonons, which was interpreted as the effect of destruction of the giant Kohn anomaly. Further evidence for an ETT came from room temperature Raman linewidth studies by Olijnyk *et al* [15]. The transverse optical zone centre phonon showed a decrease of linewidth in their measurements in the pressure interval 0–10 GPa and a sudden reversal to broadening thereafter. As the ETT could initiate electronic excitations near the region where the additional Fermi surface sheet develops to provide an extra channel of relaxation, the observed broadening supports its occurrence. The ETT-based broadening also indicates stronger electron–phonon coupling which should result in an increase in resistivity. In fact, the high-pressure resistance measurements of Lynch and Drickamer [21] showed an initial decrease, a minimum, and a *smooth* increase thereafter [5], indicating some subtle transition. However, the room temperature neutron inelastic experiments produced conflicting observations regarding the ETT, with Morgan's data supporting the destruction of the giant Kohn anomaly, whereas Klötz *et al* [11] failed to observe the expected softening. Among the theoretical calculations also, there is considerable disagreement. Some earlier calculations showed the occurrence of an L-point ETT near 10 GPa pressure; but it did not appear in later calculations, which led to the suggestion that the K-point ETT could also contribute to the weak c/a anomaly [5, 7, 10, 12, 13, 16]. In any case, the softening of phonon modes was obtained in the calculations of Li and Tse [16].

These controversies have recently led to the theoretical investigation of the effect of temperature on the ETT and the c/a anomaly in Zn, as it was earlier suspected that temperature effects would wipe out these phenomena [16]. Godwal *et al* [40] recently showed, by means of non-zero-temperature first-principles electronic structure calculations, that temperature does not hinder the occurrence of an ETT in Zn, at least at room temperature. In fact, they showed that the band structure itself changes, and these changes in Zn are such that ETT effects are enhanced. Also, the recent experiments of Takemura *et al* [18] have confirmed that the c/a anomaly is undetectable at low temperature (40 K) as well, and the deviation from the smooth decrease is less than 0.006, thus giving an upper limit to the anomaly.

The controversy for Zn about the L-point ETT near 10 GPa is continuing mainly due to the complexity of identifying the ETTs in general. The subtle nature of the transition, often without any structural change and the associated volume collapse, makes it difficult to detect. Hence, apart from the observation of direct Fermi surface changes, it is quite difficult to identify an ETT by the usual techniques employed for studies of phase transitions, such as investigating the pressure-versus-volume (P–V) equation of state (EOS), anomalies in the specific heat and susceptibility, etc. In fact, in many cases, the evidence of a Lifshitz transition has been indirect, such as when anomalies in the superconducting transition temperature are not explained by any other phenomenon [23–26].

As changes in the Fermi surface topology are involved in an ETT, transport properties are expected to show anomalies. Among them the thermoelectric power is the best property to

study to identify the signatures of a Lifshitz transition, as it depends upon the energy derivative of the density of states at the Fermi level (ϵ_F) (unlike many other physical properties which depend upon the density of states at ϵ_F) and thus should show appreciable change (as a peak) as the density of states passes through ϵ_F in a Lifshitz transition [27]. However, thermoelectric power data on most systems are difficult to analyse, as the electronic contribution could be overshadowed by those influenced by phonons and other complications [28], though in a few systems the thermoelectric power has been useful in identifying the Lifshitz transitions [29]. Other transport properties such as electrical and thermal resistances, and the thermal expansion coefficient, could also provide some subtle evidence for a Lifshitz transition, as discussed by Kechin [5] for Zn, in which the variations along principal axes under pressure and temperature changes intersect. Thus in the present study, we have revisited the variation of resistance under compression with accurate pressure measurements in a diamond anvil cell (DAC), as earlier measurements by Lynch and Drickamer [21] are old and have possible uncertainties in the pressure scale. We have extended the resistance measurements to higher pressures, and corroborated our observations with theoretical estimates using the results of first-principles electronic structure calculations.

For electrical resistance measurements, a clamp-type Merrill–Bassett DAC [30] with diamonds of culet size 400 μm was used on pure (zone-refined) samples of zinc of thickness less than 5 μm. A thin sheet of Zn was prepared by pressing a small piece of Zn between the diamond anvils of the DAC. A preindented stainless steel gasket with a 400 μm hole stuffed with alumina powder of 0.05 μm grain size was used to contain the sample. This was prepared by fixing the gasket on one of the anvils (lower anvil) and stuffing the hole with alumina and pressing it so that there is extrusion. During this precompaction, a thin Mylar (thickness 2 μm) sheet was also put over the alumina powder. This prevents the sticking of the alumina powder to the other anvil (upper anvil). Thus alumina insulates the leads and sample from the gasket. Two 20 μm parallel stainless steel wires centred on the upper anvil serve as leads for quasi-four-probe measurements. The portions of the wires over the anvil face were flattened by a tungsten carbide pin to restrict the lead movement under pressure. Fine powder of ruby filled between the wires was employed for pressure measurements by the ruby fluorescence technique. Over this, the sample was kept crossing the wires. The Mylar layer employed, being an organic material, reduces the pressure gradient considerably and produces quasi-hydrostatic pressure as seen by the sharpness of the ruby lines at least up to a pressure of 25 GPa. The broadening of the ruby was considerable when no Mylar sheet was employed. The pressure was measured at the centre of the diamond anvil by viewing the sample with a CCD detector employing a set-up with a spatial resolution better than 10 μm. The voltage drop was measured across a very small segment of the sample ($\sim$40 μm) in the centre of the diamond, so the effect of pressure inhomogeneities was minimized. The cell was slowly tightened to obtain the desired pressure, and voltage and current measurements were performed to obtain the resistance of the sample. Before each measurement, the resistance between the leads and gasket was checked to avoid collecting data after the leads had shorted with the gasket. The full details of the assembly are given elsewhere [31]. A series of measurements of the variation of the resistance with pressure were made on Zn. With increasing pressure, the resistance of the sample first decreased, and then started increasing up to 18 GPa; this was followed by a decrease up to 25 GPa, the highest pressure to which current measurements were carried out. The pressure at which the increase in the resistance is seen varies from 7.5 to 9.5 GPa from run to run. It may be noted that earlier resistance measurements to 16 GPa (on Drickamer's corrected pressure scale) also showed an increase in resistance with pressure, and an indication of its decrease at higher pressure [21]. The onset of the decrease in resistance above 20 GPa was observed to depend on the pressure soaking time; unless it is 10–20 min per pressure point, no decrease was
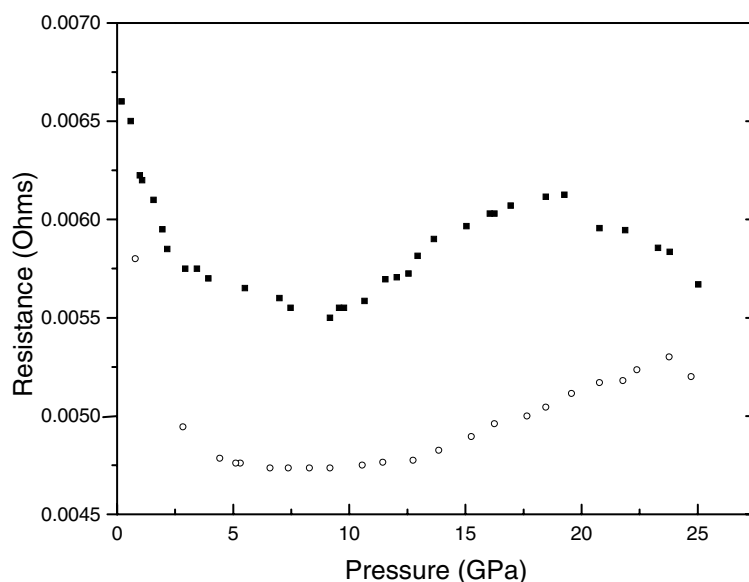
Figure 1. The measured resistance variation of zinc with pressure. The filled squares represent the loading (increasing pressure) data, whereas the unfilled circles correspond to the unloading data.

observed. When pressure is released the resistance recovers with some hysteresis. The typical behaviour of the resistance of zinc with pressure is shown in figure 1. An expected anomaly (see the discussion below) in the pressure variation of the resistance near 2 GPa is not seen in these measurements. It may be noted that this anomaly was only observed in measurements on oriented single-crystal pieces, and our measurements are on polycrystalline material.

We now describe our calculation of the resistance based on first-principles finite-temperature electronic structure calculations. Our calculations were performed by the full-potential linear augmented-plane-wave method as implemented in the WIEN97 code by Blaha *et al* [32]. We worked within the local density approximation for the exchange–correlation term in the Kohn–Sham equations [33, 34], and used a gigantic k-sampling of 115 101 k-points in the BZ. We also included the effects of the spin–orbit coupling interactions perturbatively in our calculation of the band structure. The main modification made from the zero-temperature theory is in evaluating the charge density. The effects of finite temperature have been included by populating the single-particle energy levels using the Fermi distribution function and constructing the charge densities with them in the self-consistent scheme, and considering entropy terms in obtaining the grand potential. The details of our calculation have been reported elsewhere [40] and we only state the main results here. At ambient pressure we find that the Fermi level lies in a wide and dispersive band. At the L point in the BZ there is a *local* gap and the unoccupied level is separated from the Fermi level by 10.6 mRyd. With increasing pressure this gap reduces until it reaches a minimum of 2.5 mRyd (370 K) at a pressure of 9.9 GPa, and again at higher pressures the gap increases.

With these results, and the computed density of states, we provide a qualitative explanation of the resistance minimum and its subsequent increase by attributing it to an extra contribution to the resistance coming from thermally excited electrons, which occupy states above the L-point *local* gap. We would like to point out here that earlier work by Kechin [5] qualitatively correlated the resistivity minimum and its subsequent upturn as proportional to the density of states. This can only be approximate, as it neglects changes in the carrier density and the

relaxation time of the electrons, both of which change with pressure. Moreover, the densities of states used in those calculations were obtained using the atomic sphere approximation for the crystal potential, which has its own inherent limitations. As the bands involved in the conduction process are wide and dispersive, we use the Bloch resistivity formula, derived for electrons with a parabolic dispersion scattering from acoustic Debye phonons. The Bloch expression for the resistivity for a single band, assuming a deformable potential, is given by [35]

$$\rho = \frac{3\pi\hbar Q^6 n^2}{8e^2\epsilon_F D(\epsilon_F)^2 N k_B \theta_D k_F^4} \left(\frac{T}{\theta_D}\right)^5 I_5(\theta_D/T). \tag{1}$$

Here n is the electron density, ϵ_F is the Fermi energy, Q is a phonon wavevector, $D(\epsilon_F)$ is the density of states per unit volume, θ_D is the Debye temperature, and k_F is the Fermi wavevector. The function I_5 is a Debye integral given by

$$I_5(x) = \int_0^x \frac{z^5 e^z}{(e^z - 1)^2}\, dz. \tag{2}$$

Expressing ϵ_F and k_F in terms of n and $D(\epsilon_F)$, the Bloch formula can be rewritten as

$$\rho = \frac{\pi^2 \hbar Q^6 n^{-1/2}}{4e^2 D(\epsilon_F) k_B \theta_D} \left(\frac{T}{\theta_D}\right)^5 I_5(\theta_D/T). \tag{3}$$

We assume that there are two contributions to the resistivity, one in which the relevant density of states in equation (3) is that obtained from our band structure calculations at the Fermi level, the other being the contribution of thermally excited electrons across the L-point *local* gap which have their own density of states $D(\epsilon_F + \Delta)$. We assume that the fraction of valence electrons thermally excited is $\exp(\frac{-\Delta}{k_B T})$ with the remainder contributing to the usual conduction process involving electrons at ϵ_F. We calculate the bulk modulus which is the second derivative of the free energy with respect to volume and use it to estimate the sound velocity and hence the Debye temperature θ_D. We assume isotropic compression in order to convert the resistivity into resistance. We then find that the normalized resistance is given by

$$\frac{R(P)}{R(P=0)} = \left(\frac{V_P}{V_0}\right)^{3/2} \frac{[h_0(\epsilon_F)(1 - \exp\frac{-\Delta_0}{k_B T})^{3/2} + h_0(\epsilon_F + \Delta_0)\exp\frac{-3\Delta_0}{2k_B T}]}{[h_P(\epsilon_F)(1 - \exp\frac{-\Delta_P}{k_B T})^{3/2} + h_P(\epsilon_F + \Delta_P)\exp\frac{-3\Delta_P}{2k_B T}]}$$
$$\times \left(\frac{\theta_D(0)}{\theta_D(P)}\right)^6 \frac{I_5(\theta_D(P)/T)}{I_5(\theta_D(0)/T)}. \tag{4}$$

Here h_P is the density of states per unit cell, V_P is the unit-cell volume, $\theta_D(P)$ is the Debye temperature, and Δ_P is the magnitude of the L-point gap at the pressure P. We reproduce in figure 2 our results for the normalized resistance at $T = 300$ K at which temperature the experiments have been performed. We find that after a short fall initially, there is a resistance minimum at 7.5 GPa beyond which the resistance increases, reaching a maximum at around 12 GPa. The position of the resistance minimum is in reasonable agreement with the experimental data in figure 1. The carriers in the two bands contribute differently to the conductivity, as the relevant densities of states which enter the resistivity expression (equation 3) are different for the two bands. As $h(\epsilon_F) < h(\epsilon_F + \Delta)$, the extra contribution of thermally excited electrons in the upper band is not sufficiently large to compensate for the reduction of the conductivity contribution of the lower band due to a depletion in the number of carriers there. This is responsible for the rise in the resistance seen beyond 8 GPa in figure 2. However, the increase in resistance observed experimentally at pressures larger than that corresponding to the minimum is much more rapid than the theoretical prediction. For pressures above 12 GPa the resistance predicted by our calculation again falls. This is an inevitable outcome of our calculated band structure, as the
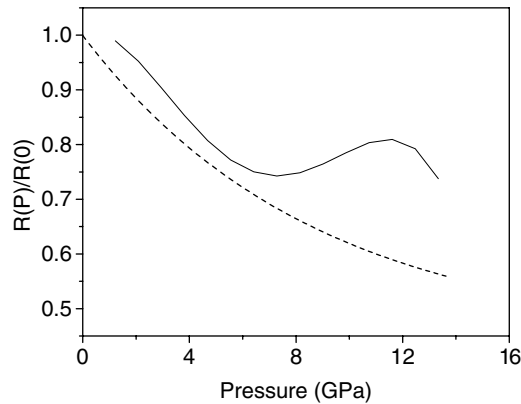
Figure 2. The calculated resistance variation of zinc with pressure (full curve). The dashed curve shows the variation obtained without considering thermal excitation of electrons.

L-point gap increases as the pressure is increased beyond 10 GPa. The initial rise as well as the fall at higher pressures seen in theory and experiment imply that the situation corresponds to a genuine ETT. The fall in the resistance measured experimentally beyond 20 GPa is most probably due to the L-point gap growing once again as the corresponding eigenvalues shift up to energies higher than ϵ_F at higher pressures. This effect is not predicted accurately by the present calculations. A calculation of the band structure incorporating interaction effects in the G–W approximation will perhaps provide a more accurate description of the observed phenomena. We have explicitly verified that considering only the conduction processes of electrons at the Fermi energy (putting $\Delta \to \infty$ in equation (4)) gives a monotonically decreasing resistance as a function of pressure. We have plotted, for comparison, in figure 2 the resistance obtained by ignoring the L-point contribution. This indicates the crucial role played by thermally excited L-point electrons in causing the resistivity upturn. The observation of large hysteresis and the indication of the slow relaxation effects in our resistance measurements suggest that other interesting isostructural phenomenon might also take place around 20 GPa (see also [18]).

We now mention some shortcomings of our calculations. The Bloch formula is strictly valid only for free electrons which are assumed to scatter off phonons only by normal (non-Umklapp) processes. Our method of estimating θ_D is approximate, as it relies on an isotropic phonon spectrum which is not the case in the hcp-structured zinc. Both of these factors could be responsible for the discrepancy between our calculated and the measured resistances. However, the trend is adequately reproduced.

Having seen the signature of an ETT in the electrical resistance, we have sought to identify it using some independent set of data. We have recently shown that P–V data, expressed in the universal equation-of-state (UEOS) [36] form, can help in identifying a Lifshitz transition [22, 29]. An ETT involves relative changes in the electron energy band population, as in the case of an s-to-d transition, and leads to change in the pressure derivative of the bulk modulus, resulting in the deviation of the UEOS from a linear variation [37]. Until recently, it has been onerous to get adequate information from the experimental UEOS, as accurate P–V data for closely spaced intervals of pressure were difficult to collect. With the availability of intense synchrotron sources, dense and precise data can now be collected to identify the signatures of ETTs [22]. We utilized such detailed published data, from Takemura [14], on Zn to identify the ETT through the UEOS.

As is well known, the UEOS is defined by
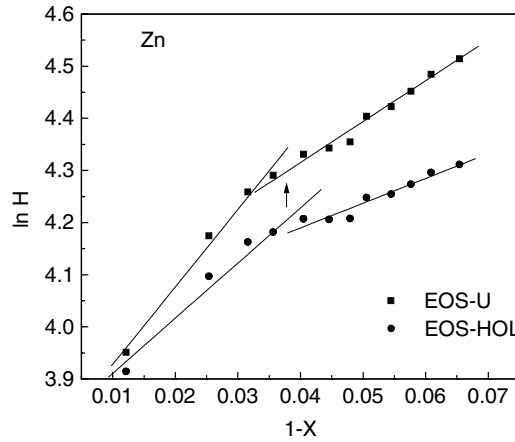
$$\ln H_{UEOS} = \ln K_0 + \eta(1 - X) \tag{5}$$

Figure 3. The universal and Holzapfel equations of state (EOS-U and EOS-HOL, respectively) of zinc. The arrow corresponds to the weak c/a anomaly near 10 GPa pressure, claimed by some experiments and theoretical calculations.

where

$$H_{UEOS} = \frac{PX^2}{3(1-X)} \tag{6}$$

$$X = (V/V_0)^{1/3}. \tag{7}$$

V is the volume at pressure P, V_0 is the ambient pressure volume, and η is related to K_0', the pressure derivative of the bulk modulus K_0, by

$$\eta = 3(K_0' - 1)/2. \tag{8}$$

The P–V data of Takemura [14] showed hardly any structure near 10 GPa [14], whereas a distinct change in slope in the UEOS (figure 3) is evident, which in the absence of structural transition is attributed to an ETT. Note that only a few data are available in the low-pressure region. Hence any possible structure due to a K-point ETT which occurs around 1.5–2 GPa cannot be seen in the curve [38].

In order to strengthen our argument regarding the anomaly seen in the UEOS, we have also analysed the same P–V data using the equation of state proposed by Holzapfel [39]. The Holzapfel (subscript HOL) equation of state is defined by

$$\ln H_{HOL} = \ln K_0 + C_2(1-X) \tag{9}$$

where

$$H_{HOL} = \frac{PX^5}{3(1-X)} \tag{10}$$

and

$$C_2 = 3(K_0' - 3)/2 \tag{11}$$

and this is also shown in figure 3, labelled as EOS-HOL. This too shows a change of slope at almost the same pressure[1].

We conclude by summarizing our main findings. The UEOS as well as the Holzapfel EOS show that an ETT occurs near 10 GPa pressure in Zn, which was difficult to identify

---

[1] We have also fitted the P–V data of Takemura [14] to the HOL form of Holzapfel's EOS [39]. The data points show deviation from the fitted curve in the region above 10 GPa pressure, indicating an anomaly in that region.

by other techniques. The variation of the resistance of Zn with pressure shows a minimum and is similar to that observed by Lynch and Drickamer. The pressure at which the resistance minimum occurs is close to the value where the ETT at the L point occurs. The theoretical calculation is able to corroborate the experimental variation of the resistance. The present study provides strong support for the occurrence of an ETT in Zn at about 10 GPa and room temperature.

References

[1] Daniuk S, Jarlborg T, Kontrym-Sznajd G, Majsnerowski J and Stachowiak H 1989 *J. Phys.: Condens. Matter* **1** 8397
[2] Meenakshi S *et al* 1992 *Phys. Rev.* B **46** 14 359
[3] Schülte O *et al* 1991 *High Pressure Res.* **6** 169
[4] Kohn W 1959 *Phys. Rev. Lett.* **2** 393
[5] Kechin V V 2001 *Phys. Rev.* B **63** 45 119
[6] Takemura K 1995 *Phys. Rev. Lett.* **75** 1807
[7] Potzel W *et al* 1995 *Phys. Rev. Lett.* **74** 1139
[8] Morgan J G *et al* 1996 *Phys. Rev.* B **54** 812
[9] Fast L *et al* 1997 *Phys. Rev. Lett.* **79** 2301
[10] Godwal B K *et al* 1997 *Phys. Rev.* B **56** 14 871
[11] Klötz S, Braden M and Besson J M 1998 *Phys. Rev. Lett.* **81** 1239
[12] Novikov D L *et al* 1997 *Phys. Rev.* **56** 7206
[13] Novikov D L *et al* 1999 *Phys. Rev.* B **59** 4557
[14] Takemura K 1999 *Phys. Rev.* B **60** 6171
[15] Olijnyk H *et al* 2000 *Phys. Rev.* B **62** 5508
[16] Li Z and Tse J S 2000 *Phys. Rev. Lett.* **85** 5130
[17] Neumann G S, Stixrude L and Cohen R E 2001 *Phys. Rev.* B **63** 54 103
[18] Takemura K, Yamawaki H, Fujihisa H and Kikegawa T 2002 *Phys. Rev.* B **65** 132107
[19] Lifshitz I M 1960 *Zh. Eksp. Teor. Fiz.* **38** 1569 (Engl. transl. 1960 *Sov. Phys.–JETP* **11** 1130)
[20] Dagens 1978 *J. Phys. F: Met. Phys.* **8** 2093
[21] Lynch R W and Drickamer H G 1965 *J. Phys. Chem. Solids* **26** 63
[22] Godwal B K *et al* 2002 *Phys. Rev.* B **65** 140101 (rapid communication)
[23] Struzhkin V V *et al* 1997 *Phys. Rev. Lett.* **79** 4262
[24] Pickett W E, Freeman A J and Koelling D D 1980 *Phys. Rev.* B **20** 2695
[25] McMahan A K 1978 *Phys. Rev.* B **17** 1521
[26] Louie S G and Cohen M L 1974 *Phys. Rev.* B **10** 3237
[27] Suslov I M 1987 *Pis. Zh. Eksp. Teor. Fiz.* **46** 26 (Engl. transl. 1987 *JETP Lett.* **46** 30)
[28] Blatt F J, Schröder P A, Foiles C L and Greig D 1976 *Thermoelectric Power of Metals* (New York: Plenum)
[29] Godwal B K *et al* 1998 *Phys. Rev.* B **57** 773
[30] Vijayakumar V and Meenakshi S *BARC Report* unpublished
[31] Garg A B, Vijayakumar V and Godwal B K 2002 in preparation
[32] Blaha P, Schwarz K and Luitz J 1999 *WIEN97, a Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* Technical University of Vienna (ISBN 3-9501031-0-4)
     This is an improved and updated Unix version of the original copyrighted WIEN code which was published by Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399
[33] Hohenberg P C and Kohn W 1964 *Phys. Rev.* B **136** 864
[34] Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133
[35] Ziman J M 1967 *Electrons and Phonons* (Oxford: Oxford University Press) p 364
[36] Rose J H, Vary J P and Smith J R 1984 *Phys. Rev. Lett.* **53** 344
[37] Sikka S K 1988 *Phys. Rev.* B **38** 8463
[38] Rao R S, Modak P and Godwal B K 2001 *Phys. Rev. Lett.* **87** 259601
[39] Holzapfel W B 1991 *Molecular Systems under High Pressure* ed R Pucci and G Piccitto (New York: Elsevier Science) p 61
[40] Godwal B K *et al* 2002 *Solid. State Commun.* submitted