Effect of the Spin-Orbit Interaction on the Thermodynamic Properties of Crystals: Specific Heat of Bismuth

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We discuss measurements and *ab initio* calculations of the specific heat for crystalline bismuth, strictly speaking, a semimetal but in the temperature region accessible to us ($T > 2$ K) acting as a semiconductor. We extend experimental data available in the literature and notice that the *ab initio* calculations without spin-orbit interaction exhibit a maximum at ~8 K, about 20% lower than the measured one. Inclusion of spin-orbit interaction decreases the discrepancy markedly: the maximum of $C(T)$ is now only 7% larger than the measured one. Exact agreement is obtained if the strength of the spin-orbit Hamiltonian is reduced by a factor of ~0.9. We also discuss the dependence of the lattice parameter and the cohesive energy on spin-orbit interaction.

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Introduction.—In the past few years, a number of investigations on the dependence of the specific heat of semiconductors and insulators on temperature and isotopic masses have been carried out. These works involved careful low temperature experiments (for elemental crystals, see Refs. [1,2], for binaries, see Refs. [3] and references therein) and elaborate *ab initio* calculations based on electronic band structures computed in the framework of the local density approximation (LDA). Recent work involving binary lead chalcogenides with different isotopic compositions [PbS (Ref. [4]), PbSe (Ref. [5])] yields a low temperature maximum in the quantity $C(T)/T^3$ (at ~12 K) [4,5] about 25% lower than the measured one. Correspondingly, the calculated phonon dispersion relations are on the average 10% higher than those determined with inelastic neutron scattering (INS) [6]. The higher phonon frequencies qualitatively explain the lower specific heats obtained from the calculations.

When trying to ascertain whether the *harder* phonon frequencies (and lower specific heats) calculated for PbS and PbSe were due to the lack of spin-orbit (SO) coupling in the *ab initio* electronic structure, some difficulties arose. These involved not only the extended computational time but also divergences in the dispersion relations of the optical phonons for $\boldsymbol{q} \rightarrow 0$. The latter may be related to the strongly ionic, nearly ferroelectric character of these compounds.

To our knowledge the computation of the $\boldsymbol{q} \rightarrow 0$ divergences when the spin-orbit coupling is present has not yet been implemented in existing first-principles codes. By contrast, for metals, there is no such divergence, which makes possible the direct computation of phonon band structure and thermodynamical properties based on density-functional perturbation theory (Ref. [7–9]), including spin-orbit, as implemented in the ABINIT software [10]. Thus, we performed measurements and calculations for crystalline bismuth, which is free of the ionic divergences present in the lead chalcogenides.

In this Letter we demonstrate that inclusion of SO coupling, in fact, considerably reduces the discrepancies between experimental heat capacity data and *ab initio* results. In addition, we also discuss the dependence of the rhombohedral lattice parameter a_0 and the cohesive energy E_c on the magnitude of the SO coupling.

Bismuth is a semimetal closely related to the lead chalcogenides: it has 10 valence electrons per primitive cell and a rhombohedral structure which can be derived from that of PbS by making both atoms equal and applying a Peierls-like distortion to the PbS cube, involving an elongation of one of its [111] axes [11]. The distortion converts the simple cubic structure of bismuth, with one atom per primitive cell, into a rhombohedral one with two atoms per primitive cell (two sublattices). This structure is characterized by three parameters: the bond length a_0, the rhombohedral angle, and a shift between the two sublattices [12,13]. These parameters were determined by energy minimization using the ABINIT code. The results obtained for these parameters in Refs. [12,13] with and without SO coupling differ by less than 1%.

The phonon dispersion relations were calculated with ABINIT in Ref. [12] with SO coupling whereas in Ref. [13] calculations with and without SO coupling were performed. With SO coupling, excellent agreement with experimental results (Ref. [14]) was obtained whereas without it, discrepancies of the order of 10% were found, the calculated bands lying higher in frequency than the measured ones. Similar results were found for PbS (Ref. [4]) and PbSe (Ref. [5]) without SO coupling. In view of these results, we proceeded to calculate the specific heat $C(T)$ of bismuth. In order to complete the available experimental data (carried out on polycrystalline samples) [15–19] we also performed measurements on high purity (99.9999%, Preussag Pure Metals) single crystals. Recent data collected by various earlier authors and our own data (our experimental technique is described in Refs. [1–4]) are compiled in Fig. 1, together with the results of our *ab initio* calculations performed with and without spin-orbit coupling.

Results and discussion.—The hitherto available experimental points were measured on polycrystalline samples. They are rather widely spaced in temperature, with the exception of Keesom's below 4 K (Ref. [16,20]). We have therefore performed measurements of $C_p(T)$ on single crystals for T between 1.8 and 100 K with the measuring temperatures spaced by ~0.1 K up to 50 K and 0.5 K steps above 50 K. The maximum of $C(T)/T^3$ takes place at 7.5 K. According to Ref. [5] it should be found at $\sim T_{TA}/6$, where $T_{TA} \sim 42$ K is an Einstein oscillator frequency which can be read off the phonon density of states [12]. The temperature of the maximum in Fig. 1 is found to be 7.5 K, fairly close to $T_{TA}/6 = 7$ K.

Our measurements place the maximum value of C/T^3 at 2.320 ± 0.03 mJ/mol K^4. The value calculated without SO splitting lies at 1.940 mJ/mol K^4 whereas with SO coupling one finds 2.500 mJ/mol K^4. Hence, the results of the calculation without SO coupling lie 20% below the experimental data; those with SO coupling lie only 7% above. Not only is the difference between measured and calculated values of C/T^3 3 times smaller when SO interaction is taken into account, but the agreement with SO coupling above 12 K lies within the experimental error, whereas without SO coupling a considerable difference is found.

This improvement illustrates the importance of SO interaction for the calculations of thermodynamic properties starting from *ab initio* electronic band structures for systems containing heavy atoms and confirms our conjecture that similar discrepancies between calculated and measured values of C/T^3 found for PbS and PbSe [4,5] must be due to the lack of SO coupling in the electronic structure calculations. These results suggest performing calculations and measurements for antimony (also a semimetal with the same crystal structure as Bi) which has a considerably smaller atomic SO coupling than bismuth (0.84 versus 1.7 eV).

While the Sb work is in progress, we have pursued yet another avenue: we have multiplied the spin-orbit coupling Hamiltonian by a factor $0 < \lambda < 1$ and repeated the full *ab initio* calculations of $C(T)$ for several values of λ. The results obtained for bismuth are shown in Fig. 2.

This figure reveals the strongly supralinear dependence of the SO effect on C/T^3 which can be fitted with the expression

$$C/T^3 = c_0[1 + c_2\lambda^2(1 + c_4\lambda^2)] \qquad (1)$$

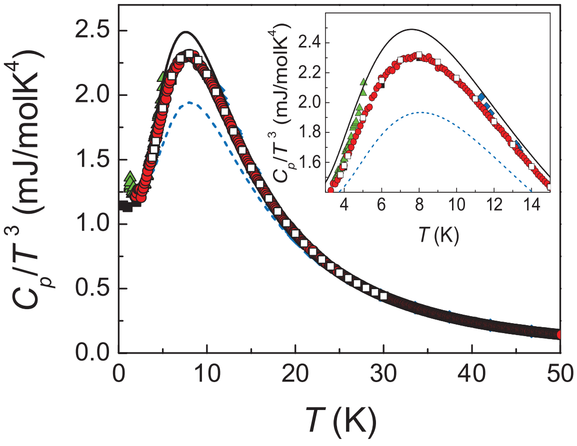

FIG. 1 (color). Heat capacity of a Bi single crystal, purity 99.9999%. (Red filled) circles as measured in this work compared with literature data obtained on polycrystalline samples. (Green) ▲ (Ref. [16]); (blue) ◆ (Ref. [17]); □ (Ref. [18]); (black) ■ (Ref. [19]). (Black) solid line: ABINIT results with spin-orbit coupling included; (blue) dashed line: ABINIT calculation without spin-orbit coupling.

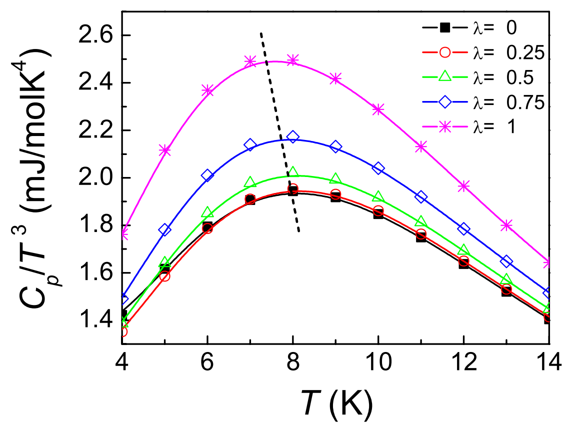

FIG. 2 (color online). Calculated heat capacities of Bi with varying magnitude of the SO coupling as indicated in the inset. Note that the maximum shifts to lower temperatures (inclined dashed line) with increasing SO coupling, as it corresponds to decreasing phonon frequencies (see text).

with $c_0 = 1.942(2)$ mJ/mol K^4, $c_2 = 0.116(7)$, and $c_4 = 1.46(13)$.

The fit is displayed in Fig. 3(a). For $\lambda = 1$ the fourth order term surpasses the quadratic term. Exact agreement between the measured and the calculated values of C/T^3 is obtained if one reduces the SO coupling by the factor $\lambda = 0.9$.

It is expected that other mechanical and thermodynamic properties of Bi should depend on the SO coupling as well, i.e., on the value of λ. The simplest of them is probably the rhombohedral lattice parameter a_0. It is shown in Fig. 3(b) calculated for the same values of λ as $C(T)$ and fitted with an expression similar to Eq. (1) with $a_0(\lambda = 0) \equiv c_0 = 4.6529(7)$ Å, $a_2 = 0.0069(9)$, and $a_4 = 0.29(16)$. The values of the fit parameters c_i indicate that there is no simple relationship between the effect of SO splitting on $C(T)$ and the lattice parameter $a_0(\lambda)$. The effect of spin-orbit interaction on $C(T)$, as described by c_2 and c_4, is much larger than that on the lattice parameter $a_0(\lambda)$. For $\lambda = 1$, however, the calculated value for a_0 (4.694 Å) is also much closer to the experimental one (4.720 Å) than that obtained for $\lambda = 0$ (4.652 Å).

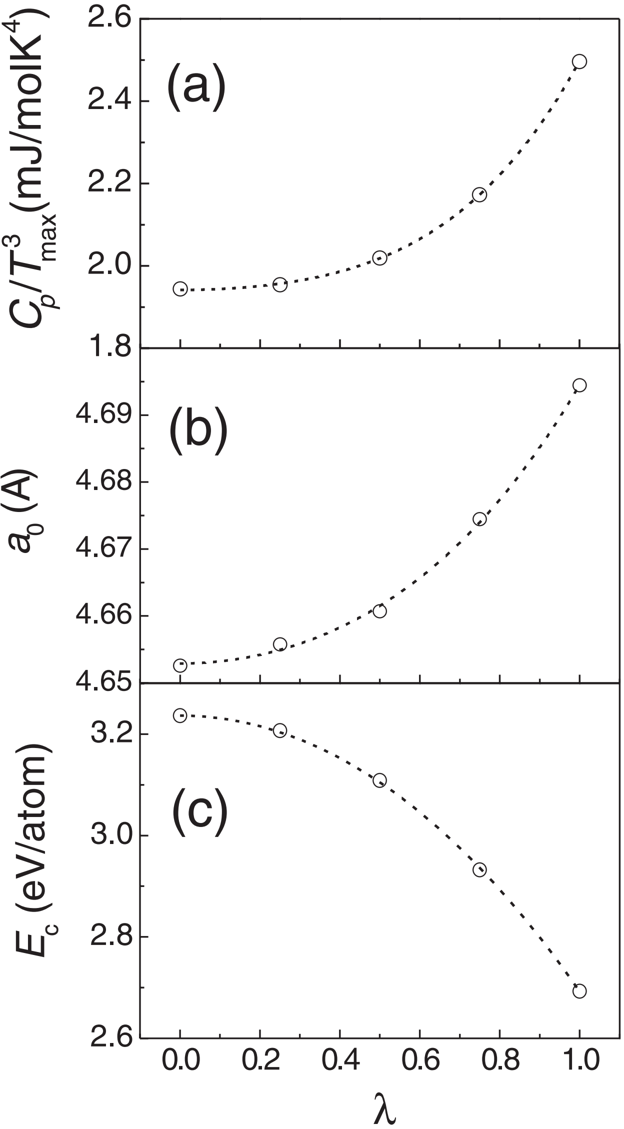

FIG. 3. (a) Maxima of the quantity $C_p(T_{\max})/T_{\max}$ vs spin-orbit coupling parameter λ. (b) Energy minimized lattice parameter a_0 vs spin-orbit coupling parameter λ. (c) Cohesive energy of bismuth vs λ, calculated as discussed in the text. The circles (○) represent our calculations, the dashed lines fits with Eq. (1) which lead to the parameters given in the text.

We have also calculated the cohesive energy E_c for several values of λ. E_c was obtained as the difference between the calculated total energy for the free atom and that for the solid, both calculated with the LDA approximation for exchange and correlation using ABINIT and spinorial, spin-polarized wave functions. This procedure leads to the λ dependence of E_c shown in Fig. 3(c). $E_c(\lambda)$ can also be fitted with Eq. (1), leading to the parameters $c_0 = 3.236$ eV/atom, $c_2 = -0.161(4)$, and $c_4 = 0.045(26)$. Hence, like for the other thermodynamic properties investigated, no linear term in λ appears in E_c. The lack of linear terms in λ in the thermodynamic properties contrasts with the results of the calculations for individual one-electron states [21]. This leads to the conclusion that upon integration of all one-electron states the linear terms cancel and only terms of second or higher order in λ remain.

Note that the inclusion of spin-orbit coupling considerably improves the agreement of calculated and measured values of E_c. The calculated value $E_c(\lambda = 1) = 2.76$ eV is remarkably close to the measured one ($E_c = 2.16$ eV/atom (Ref. [22])), especially when one considers that it is obtained as the difference of two large energies, of the order of 150 eV/atom.

In conclusion, we have investigated the effect of SO interaction on three thermodynamic properties, $C(T)$, a_0, and E_c, of a solid consisting of the heavy element bismuth. Such effects, apparently rather substantial for a first-principles calculation of the physical properties, have not received much consideration in the literature so far. For a discussion of other similar phenomena, see Refs. [23,24].

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Note added in proof.—The fit with Eq. (1) implicitly implies the absence of cubic terms in λ. In order to check this assumption, we have calculated the quantities in Fig. 3 for negative values of λ and found, e.g., that a_0 ($\lambda = +1$) differs slightly from a_0 ($\lambda = -1$). A fit with the equation $a_0(\lambda) = a_0(0)[1 + c_2\lambda^2(1 + c_3\lambda)]$ yields $a_0(0) = 4.6528(5)$ Å, $c_2 = 0.0064(2)$, and $c_3 = 0.41(2)$ indicating that cubic terms play an important role.

[1] M. Cardona, R. K. Kremer, M. Sanati, S. K. Estreicher, and T. R. Anthony, Solid State Commun. **133**, 465 (2005).
[2] A. Gibin, G. G. Devyatykh, A. V. Gusev, R. K. Kremer, M. Cardona, and H.-J. Pohl, Solid State Commun. **133**, 569 (2005).
[3] J. Serrano, R. K. Kremer, M. Cardona, G. Siegle, A. H. Romero, and R. Lauck, Phys. Rev. B **73**, 094303 (2006).
[4] M. Cardona, R. K. Kremer, R. Lauck, G. Siegle, J. Serrano, and A. H. Romero, Phys. Rev. B **76**, 075211 (2007).
[5] M. Cardona, R. K. Kremer, R. Lauck, G. Siegle, J. Serrano, and A. H. Romero (to be published).
[6] M. M. Elcombe, Proc. R. Soc. A **300**, 210 (1967).
[7] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).
[8] C. Lee and X. Gonze, Phys. Rev. B **51**, 8610 (1995).
[9] X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J. Y. Raty, and D. C. Allan, Comput. Mater. Sci. **25**, 478 (2002).
[10] ABINIT is a common project of the Université Catholique de Louvain, Corning Incorporated, and others (http://www.abinit.org).
[11] R. Bellisent, C. Bergman, A. Pellegati, R. Ceolin, and J. P. Gaspard, J. Non-Cryst. Solids **97–98**, 1263 (1987).
[12] E. D. Murray, S. Fahy, D. Prendergast, T. Ogitsu, D. M. Fritz, and D. A. Reis, Phys. Rev. B **75**, 184301 (2007).
[13] L. E. Díaz-Sánchez, A. H. Romero, and X. Gonze, Phys. Rev. B (to be published).
[14] J. L. Yarnell, J. L. Warren, R. G. Wenzell, and S. H. Koenig, IBM J. Res. Dev. **8**, 234 (1964).
[15] For a compilation of heat capacity data of polycrystalline Bi published before 1964, see Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Matter* (Plenum, New York, 1970), Vol. 4.
[16] P. H. Keesom, Phys. Rev. **96**, 897 (1954).
[17] P. Franzosini and K. Clusius, Z. Naturforsch. **19a**, 1430 (1964).
[18] T. C. Cetas, J. C. Holste, and C. A. Swenson, Phys. Rev. B **182**, 679 (1969).
[19] D. G. Archer, J. Chem. Eng. Data **40**, 1015 (1995)
[20] Measurements below ~2 K have been carried out by N. E. Phillips, Phys. Rev. **118**, 644 (1960); and subsequently by H. K. Collan, M. Krusius, and G. R. Pickett, Phys. Rev. B **1**, 2888 (1970) in order to establish the electronic and the nuclear quadrupole contribution to the heat capacity of Bi.
[21] X. Gonze, J.-P. Michenaud, and J. P. Vigneron, Phys. Rev. B **41**, 11 827 (1990).
[22] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1968), p. 78, 3rd ed.
[23] L. J. Norrby, Journal of Chemical Education **68**, 110 (1991).
[24] P. Pyykkö, Chem. Rev. **88**, 563 (1988).