Effect of the spin-orbit interaction on the thermodynamic properties of crystals: The specific heat of bismuth

Díaz-Luis
CINVESTAV-Querétaro, Libramiento Norponiente 2000, Fraccionamiento Real de Juriquilla 76230 Querétaro, Qro. Mexico
and Unité de Physico-Chimie et de Physique des Matériaux Université Catholique de Louvain B-1348 Louvain-la-Neuve, Belgium

A.H. Romero
CINVESTAV-Querétaro, Libramiento Norponiente 2000, Fraccionamiento Real de Juriquilla 76230 Querétaro, Qro. Mexico

M. Cardona and R. K. Kremer
Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

X. Gonze
Unité de Physico-Chimie et de Physique des Matériaux Université Catholique de Louvain B-1348 Louvain-la-Neuve, Belgium

(Dated: February 1, 2008)

In recent years, there has been increasing interest in the specific heat $C$ of insulators and semiconductors because of the availability of samples with different isotopic masses and the possibility of performing ab initio calculations of its temperature dependence $C(T)$ using as a starting point the electronic band structure. Most of the crystals investigated are elemental (e.g., germanium) or binary (e.g., gallium nitride) semiconductors. The initial electronic calculations were performed in the local density approximation and did not include spin-orbit interaction. Agreement between experimental and calculated results was usually found to be good, except for crystals containing heavy atoms (e.g., PbS) for which discrepancies of the order of 20% existed at the low temperature maximum found for $C/T$. It has been conjectured that this discrepancies result from the neglect of spin-orbit interaction which is large for heavy atoms ($\Delta_0 \sim 1.3$eV for the p valence electrons of atomic lead). Here we discuss measurements and ab initio calculations of $C(T)$ for crystalline bismuth ($\Delta_0 \sim 1.7$ eV), 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 $\sim 8$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 spin-orbit hamiltonian is reduced by a factor of $\sim 0.8$.

I. 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] and 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 $\sim 12$K) 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). The higher phonon frequencies qualitatively explain the lower calculated specific heats.

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 ($s-o$) 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 $q \rightarrow 0$. The latter may be related to the strongly ionic, near ferroelectric character of these compounds.

To our knowledge the computation of the $q \rightarrow 0$ divergences when the spin-orbit coupling is present has not yet been implemented in existing first-principle software. 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. [6-10], including spin-orbit, as implemented in the ABINIT software). 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 s-o coupling, in fact, considerably reduces the discrepancies be-
between experimental heat capacity data and \textit{ab initio} results. In addition, we also discuss the dependence of the rhombohedral lattice parameter \(a_0\) on the magnitude of \(s-o\) 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. 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. These parameters were determined by energy minimization using the ABINIT code. The results obtained for these parameters in Refs. \ref{12} and \ref{13} with and without \(s-o\) coupling differ by less than 1%.

The phonon dispersion relations were calculated with ABINIT in Ref. \ref{12} with \(s-o\) coupling whereas in Ref. \ref{13} calculations with and without \(s-o\) coupling were performed. With \(s-o\) coupling, excellent agreement with experimental results 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. \ref{1}) and PbSe (Ref. \ref{3}) without \(s-o\) coupling. In view of these results we proceeded to calculate the specific heat \(C(T)\) of bismuth. Measurements which were performed on high purity (99.9999%, Preussag Pure Metals) single crystals in order to complete the available experimental results of our \textit{ab initio} calculations with and without \(s-o\) coupling.

Recent data collected by various earlier authors and our own data (the experimental technique is described in Refs. \ref{16,17,18,19}) are compiled in Fig. \ref{fig:1} together with the results of our \textit{ab initio} calculations performed with and without spin-orbit coupling.

![FIG. 1: (Color online) 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. \ref{16}); (blue) ● (Ref. \ref{17}); □ (Ref. \ref{18}); (black) ■ (Ref. \ref{19}). (black) solid line: ABINIT results with spin-orbit coupling included; (blue) dashed line: ABINIT calculation without spin-orbit coupling.](image1.png)

II. 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\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 \(\sim 0.1\)K up to 50K and 0.5K steps above 50K. The maximum of \(C(T)/T^3\) takes place at 7.5 K. According to Ref. \ref{3} 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. The temperature of the maximum in Fig. \ref{fig:1} is found to be 7.5 K, fairly close to \(T_{TA}/6 = 7\) K.

Our measurements place the maximum value of \(C(T)/T^3\) at 2.320 \pm 0.03 mJ/mol K\(^4\). The value calculated without \(s-o\) splitting lies at 1.940 mJ/mol K\(^4\) whereas with \(s-o\) coupling one finds 2.500 mJ/mol K\(^4\). Hence, the calculation without \(s-o\) coupling lies 27% below the experimental data, that with \(s-o\) coupling only 7% above. Not only is the difference between measured and calculated values of \(C(T)/T^3\) three times smaller when \(s-o\) interaction is taken into account, but the agreement with \(s-o\) coupling above 12 K lies within the experimental error, whereas without \(s-o\) coupling a considerable difference is found.

![FIG. 2: (Color online) Calculated heat capacities of Bi with varying magnitude of the \(s-o\) coupling as indicated in the inset. Note that the maximum shifts to lower temperatures (inclined dashed line) with increasing \(s-o\) coupling, as corresponds to decreasing phonon frequencies (see text).](image2.png)
This improvement illustrates the importance of s-o interaction for the calculations of thermodynamic properties starting from \textit{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 are also due to the lack of s-o 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 s-o coupling than bismuth (0.84 vs. 1.7eV).

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 \textit{ab initio} calculations of $C(T)$ for several values of $\lambda$. The results obtained for bismuth are shown in Fig. 2.

In conclusion, we have investigated the effect of s-o interaction on two thermodynamic properties, $C(T)$ and $a_0$ 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 also Refs. 22 and 23.

Acknowledgments

The authors acknowledge useful discussion with J. Serrano and L. Wirtz. We thank C. Busch for providing the single crystal of Bi and G. Siegle for experimental assistance. One of the authors (X.G.) would like to acknowledge support from the F.R.F.C., project N 2.4502.05. A.H.R. acknowledges support by CONACYT Mexico under Grant No. J-42647-F and D.-L. under Grant 167176. We would like also to thank the Centro Nacional de Supercomputo at IPICYT, Mexico for allocation of computer time.

This figure clearly reveals the strongly supralinear dependence of the s-o effect on $C/T^3$ which can be fitted with the expression

$$C/T^3 = c_0[1 + c_2 \lambda^2(1 + c_4 \lambda^2)]$$  \hspace{1cm} (1)

with $c_0=1.942(2)$ mJ/molK$^4$, $c_2=0.116(7)$ 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 s-o coupling by the factor $\lambda=0.8$.

It is expected that other mechanical and thermodynamic properties of Bi should depend on the s-o coupling as well, i.e., on the value of $\lambda$. 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 $\lambda$ 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 s-o 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 the experimental one (4.720 Å) than that obtained for $\lambda=0$ (4.652 Å).

In conclusion, we have investigated the effect of s-o interaction on two thermodynamic properties, $C(T)$ and $a_0$ 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 also Refs. 22 and 23.

Acknowledgments

The authors acknowledge useful discussion with J. Serrano and L. Wirtz. We thank C. Busch for providing the single crystal of Bi and G. Siegle for experimental assistance. One of the authors (X.G.) would like to acknowledge support from the F.R.F.C., project N 2.4502.05. A.H.R. acknowledges support by CONACYT Mexico under Grant No. J-42647-F and D.-L. under Grant 167176. We would like also to thank the Centro Nacional de Supercomputo at IPICYT, Mexico for allocation of computer time.

1 M. Cardona, R.K. Kremer, M. Sanati, S.K. Estreicher, T.R. Anthony, Solid State Commun. 133, 465 (2005).
2 A. Gibin, G.G. Devyatikh, 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, (unpublished).
5 M. Cardona, R.K. Kremer, R. Lauck, G. Siegle, J. Serrano, and A.H. Romero, cond-mat/0705.1804.
6 M.M. Elcombe, Proc. Roy. Soc. (London), A300, 210 (1967).
7 S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001).
8 C. Lee, X. Gonze, Phys. Rev. B 51, 8610 (1995).
9 ABINIT is a common project of the Université Catholique de Louvain, Corning Incorporated, and others (URL: http://www.abinit.org).
10 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).
11 R. Bellisent, C. Bergman, A. Pellegati, R. Ceolin, and J. P. Gaspard, J. non-cryst. Solids 97-98, 1263 (1987).
12 É.D. Murray, S. Fahy, D. Prendergast, T. Ogitsu, D. M. Fritz and D.A. Reis, Phys. Rev. B, in press.
13 Díaz-Luis, A. H. Romero, and X. Gonze, (unpublished).
14 J. L. Yarnell, J. L. Warren, R. G. Wenzell, and S. H. Koenig, IBM J. of Research and Development 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, Volume 4, (Plenum, New York, Washington 1970).
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 ~2K 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 F. Herman and S. Skillman, Atomic Structure Calculations (Prentice Hall, Englewood Cliffs, NJ, 1963).
22 L. J. Norrby, J. Chem. Education 68, 110 (1991).
23 P. Pyykkö, Chem. Rev. 88, 563 (1988).