

Effect of the spin-orbit interaction on the thermodynamic properties of crystals

M. Cardona and R.K. Kremer; L.E. Díaz-Sánchez and A.H. Romero (Querétaro, Mexico);
X. Gonze (Louvain-la-Neuve, Belgium); J. Serrano (ESRF Grenoble, France)

In the past years we have carried out a series of experiments as well as *ab initio* calculations of the dependence of the specific heat of semiconductors and insulators on temperature and isotopic masses. Recent results on the binary lead chalcogenides PbS and PbSe revealed marked differences between the calculated and the experimental heat capacities and the phonon dispersion relations [1]. This finding raised the question of whether these discrepancies were due to the lack of spin-orbit (*s-o*) coupling in the *ab initio* electronic structure calculations.

To avoid computational problems especially arising from $\mathbf{q} \rightarrow 0$ divergences of the optical phonons related to the strongly ionic, nearly ferroelectric character of PbS and PbSe we extended our studies to metals and reinvestigated in detail the low-temperature heat capacities of high purity single crystals of Bi and calculated the phonon band structures and thermodynamical properties based on Density-Functional Perturbation Theory, including spin-orbit interaction. To compare with a closely related system, albeit with significantly reduced spin-orbit coupling, we performed heat capacity measurements and *ab initio* calculations also for antimony.

Bismuth and antimony are semimetals closely related to the lead chalcogenides. They have 10 valence electrons per primitive cell and a rhombohedral structure which can be derived from the structure 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 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. The results obtained for these parameters with and without *s-o* coupling differ by less than 1%. By including *s-o* coupling, excellent agreement with experimental phonon dispersion relations for Bi

was obtained whereas without *s-o*, the calculated bands lying higher in frequency than the measured ones (not shown here).

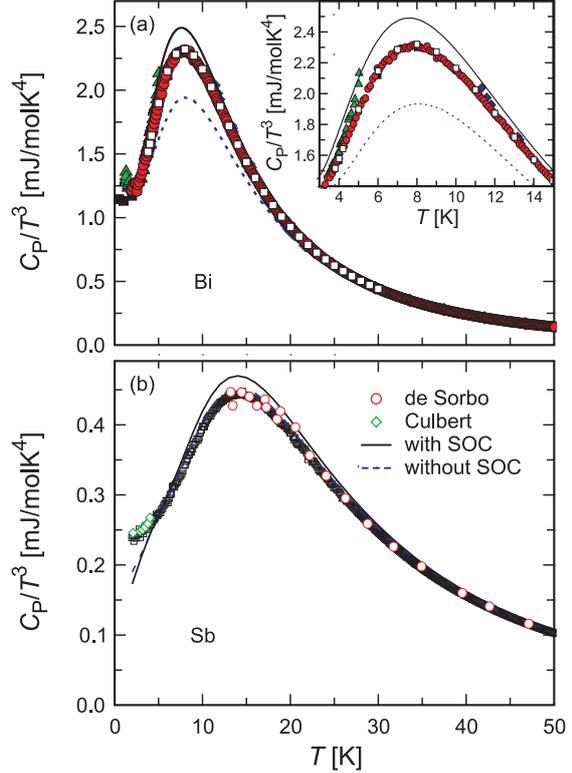


Figure 1: (a) Heat capacity of a Bi single crystal, purity 99.9999% [2]. Red filled circles compared with literature data obtained on polycrystalline samples. Black solid line: *ab initio* results with spin-orbit coupling included and without spin-orbit coupling (blue) dashed line. (b) Temperature dependence of the specific heat of Sb (open squares) are compared with data from the literature (see inset) [3] and with *ab initio* calculations with (black, solid) and without (blue, dashed) spin-orbit interaction (SOC).

Figure 1 displays a comparison of the experimental heat capacities of Bi and Sb with the calculated heat capacities with and without inclusion of *s-o* coupling. For Bi the discrepancies between experimental and calculated data (without *s-o* coupling) are largest near 10 K where the maximum in the quantity $C(T)/T^3$ occurs. The differences are significantly reduced if *s-o* coupling is included, the calculated curve now lying by about 7% higher than

the experimental data. For the lighter element Sb the difference between calculated data with and without s - o coupling is less pronounced ($\approx 4\%$). The experimental data agree rather well with the data obtained without inclusion of s - o coupling.

In order to follow and quantify the effects of s - o interaction on the maximum in C_p/T_{\max}^3 , the rhombohedral lattice parameter a_0 and the cohesive energy E_c , we varied the spin-orbit interaction by multiplying the s - o coupling Hamiltonian by a factor $-1 < \lambda < 1$, and repeated the full *ab initio* calculations for several values of λ . The results are summarized in Figs. 2 and 3.

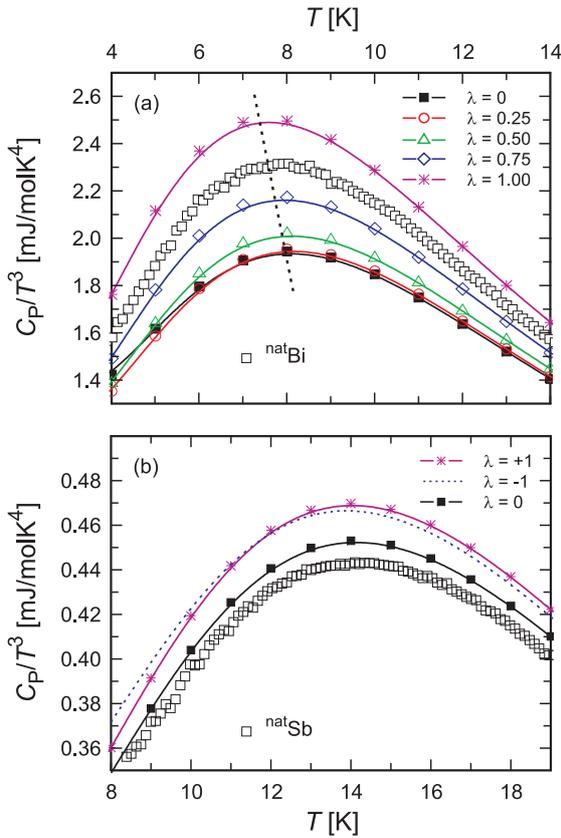


Figure 2: Measured and calculated heat capacities of Bi (a) and Sb (b). The calculations were performed with varying magnitude of the s - o coupling as indicated in the inset. Note that the maximum shifts to lower temperatures (inclined dashed line) with increasing s - o coupling, as corresponds to decreasing phonon frequencies (see text). The symbols show our experimental data, whereas the curves display the results of the calculations with various values of λ as specified in the insets.

As noted above, the effects of s - o coupling on the calculated heat capacities of Bi are essential. The discrepancy in the maximum of C_p/T_{\max}^3 calculated with and without s - o coupling amounts to $\approx 25\%$. The maximum of

C_p/T_{\max}^3 shifts to lower temperatures with increasing s - o coupling corresponding to decreasing phonon frequencies, an effect which has also been seen in the experimentally determined phonon dispersion relations. Best agreement of the experimental with the calculated heat capacity data is obtained with $\lambda \approx 0.8$.

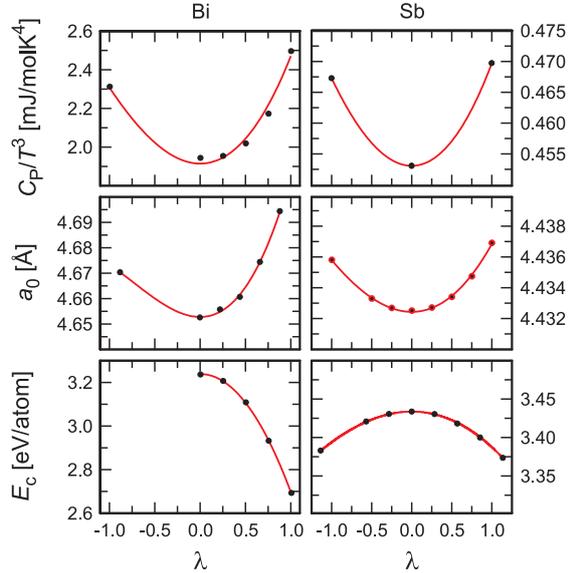


Figure 3: From top to bottom: Maxima of the quantity $C_p(T_{\max})/T_{\max}^3$ vs. s - o coupling parameter λ , energy minimized lattice parameter a_0 vs. s - o coupling parameter λ and cohesive energy of bismuth versus λ , calculated as discussed in the text. The circles (\circ) represent the results of our calculations, the dashed lines which lead to the parameters listed in the Tab. 1.

Figure 3 reveals the strongly supralinear dependence of the s - o effect on C/T_{\max}^3 , the lattice constant a_0 and the cohesive energy E_c as a function 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. All calculated quantities show a quasi-parabolic dependence on λ , with a small but nevertheless significant contribution of a cubic term and can be well-fitted to the expression, $\propto c_0 [1 + c_2 \lambda^2 (1 + c_3 \lambda)]$. The fitted coefficients c_i are compiled in Tab. 1.

The absence of a linear term in λ is expected from the fact that the expansion of the s - o Hamiltonian in λ using perturbation theory contains terms only in λ^2 and higher orders, since linear terms in λ would imply a splitting between z -components of the spin upon the s - o interaction, a splitting that can only happen in the presence of a magnetic field.

Table 1:

Fit parameters c_i obtained by fitting a cubic polynomial (see text) to the calculated heat capacity maximum C_p/T_{\max}^3 , the lattice parameter a_0 , and the cohesive energy E_c .

Quantity	Element	c_0	c_2	c_3
C_p/T_{\max}^3 [J/molK ⁴]	Bi	1914(23)	0.25(2)	0.17(5)
	Sb	453	0.034	0.079
a_0 [Å]	Bi	4.6528(5)	0.0064(2)	0.41(2)
	Sb	4.4324(1)	0.00089(2)	0.14(1)
E_c [eV/atom]	Bi	3.238(3)	-0.159(8)	0.058(52)
	Sb	3.4337(3)	-0.0162(2)	0.088(7)

Note that the square root of the ratio of the coefficients corresponding to the quadratic term in λ for the fits of a_0 and E_c of Bi and Sb, 2.7 and 3.1 respectively, is qualitatively similar to that of the s - o splitting, i.e., $1.7/0.7 = 2.42$. This relation, which also holds for the dependence of the maximum value of C/T^3 on λ , implies a simple scaling of the effects of s - o interaction on the vibrational properties.

Following the same argument we conclude that the cube root of the ratio of $c_2 \times c_3$ for Bi to $c_2 \times c_3$ for Sb should also be close to the corresponding ratio of s - o splittings (2.42). Using the values of these coefficients given in Tab. 1 we find an average value (for the three quantities in the table) of the cube root of the ratios of $c_2 \times c_3$ equal to 1.9, also close to the corresponding ratio of s - o splittings.

In conclusion, we have investigated the effect of s - o interaction on three thermodynamic properties, $C(T)$, a_0 , and E_c , of the heavy element bismuth and compared them with those of the

lighter isostructural element antimony. s - o coupling effects, apparently rather substantial for a first-principles calculation of the physical properties of solids, have not received much consideration in the literature so far. Their inclusion significantly reduces the discrepancies, e.g., between the experimental and calculated heat capacities of bismuth thus illustrating the importance of s - o interaction for the calculations of thermodynamic properties starting from *ab initio* electronic band structures for systems containing heavy atoms. These findings confirm our conjecture that similar discrepancies found for PbS and PbSe must be due to the lack of s - o coupling in the electronic structure calculations.

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- [1] Cardona, M., R.K. Kremer, R. Lauck, G. Siegle, J. Serrano and A.H. Romero. Physical Review B **76**, 075211 (2007) and unpublished results.
 - [2] Díaz-Luis, L.E., A.H. Romero, M. Cardona, R.K. Kremer and X. Gonze. Physical Review Letters **99**, 165504 (2007).
 - [3] Serrano, J., R.K. Kremer, M. Cardona, G. Siegle, L.E. Díaz-Sánchez and A.H. Romero. Physical Review B **77**, 054303 (2008).