

An investigation of the phase transition in SmSe using the fully relativistic Korringa-Kohn-Rostoker model

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 9581

(<http://iopscience.iop.org/0953-8984/1/48/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 21:09

Please note that [terms and conditions apply](#).

An investigation of the phase transition in SmSe using the fully relativistic Korringa–Kohn–Rostoker model

A Caldas[†], C A Taft[†] and H N Nazareno[‡]

[†] Centro Brasileiro de Pesquisas Físicas, Rua Dr Xavier Sigaud, 150 Urca, 22290 Rio de Janeiro, RJ, Brazil

[‡] Departamento de Física, Universidade de Brasília, 70910 Brasília, DF, Brazil

Received 11 October 1988, in final form 20 January 1989

Abstract. We report in this paper results of a relativistic *ab initio* band-structure calculation via the KKR method for the SmSe compound with the NaCl structure in the semiconductor and metallic phases. The exchange potential was taken in the free-electron Slater approximation. We have solved the full Dirac equation in the interior of the ‘muffin-tin’ spheres. The energies were evaluated at several symmetry points and other general points in the one-fortyeighth wedge of the FCC Brillouin zone. The energy bands were also calculated in the Γ –X directions for several values of the volume, indicating f–d hybridisation. The semiconductor-to-conductor phase transition is discussed in terms of the band structure obtained.

1. Introduction

The Sm solid state compound SmSe belongs to a general class of solid state compounds, i.e. the NaCl-structured monochalcogenides, which contain an exceedingly rich diversity of solid state properties representing just about every range of electrical conductivity, from good metals to wide-gap semiconductors (Allen *et al* 1979, Robinson 1979, Battlog *et al* 1976, Davis 1977, Jayaraman 1970, Ramirez *et al* 1970, Jefferson and Stevens 1978, Lawrence *et al* 1981). The differences and similarities in the physical properties of this class of rare-earth compounds should be directly related to the compound’s electronic band structure. A common characteristic of these compounds is that they have very high specific heats γ which would imply the presence of a narrow band of quasi-particles near the Fermi level. Another manifestation of a narrow-band system is given by the values of other thermodynamic properties such as thermal expansion and elastic constants. In addition the formulation of a definite theory of intermediate valence, which is exhibited by the Sm monochalcogenides has still not been achieved, although much advance has been made in this field in recent years. For theoretical models that give an insight into these interesting phenomena see, e.g., Varma (1976), Jefferson and Stevens (1978), Martin and Allen (1979) and Kuramoto and Müller-Hartmann (1981).

SmSe is a semiconductor under normal conditions having a band gap of 0.46 eV which does not order magnetically, presumably because it has a $4f^6$ Sm site configuration with a ground-state multiplet 7F_0 . One of the most interesting properties of this compound is that it undergoes a pressure-induced semiconductor-to-metal transition. The pressure required for the transition increases from 6.5 kbar for SmS to the vicinity of

40 kbar for SmSe, taking place continuously over a broad pressure range with a striking colour change from black in the low-pressure semiconducting phase to tan in the collapsed metallic phase.

In our previous work, we investigated the fully relativistic band structures of SmTe and SmS and noted that the relativistic effects such as spin-orbit coupling and mass-velocity and Darwin corrections should not be neglected in the investigation of the band structure of the heavy rare-earth systems (Nazareno *et al* 1983, Caldas *et al* 1986).

In the present work the KKR relativistic bands of SmSe are presented for various values of the lattice parameter and a plausible model that could explain its semiconductor-to-conductor phase transition is discussed in terms of the band structure obtained.

2. The relativistic KKR calculation

The lattice of ordered SmSe is of the NaCl type. In this case, we have to deal with two atoms per unit cell and the corresponding zone is FCC. We have constructed the 'muffin-tin' potential scaled by the exchange parameter α and superimposed atomic charge densities obtained from our self-consistent HFD Slater calculation from Sm and Se atoms. Since SmSe at normal pressures is non-magnetic, we have assumed in our calculations a configuration $4f^6$ for the Sm ion. The lattice parameter was taken to be 6.22 \AA for SmSe. The α expansion was performed over 14 shells of neighbours. The muffin-tin radii R_i were determined from the intersections of the potential curves $V_i(|R - R_i|)$ centred around the i th atom in the unit cell. The nearest-neighbour distances R_{SmSe} for normal pressure were about 5.88 au. The constant potential outside the spheres at normal pressure was taken to be $V_0 = 0.53 \text{ Ryd}$. (The energies were referred to a zero at the constant potential.) The muffin-tin potential is stronger in the interior of the Sm sphere, which allows a certain amount of charge transfer into the Sm positions. We have not taken this effect into account in the present calculations. In solving the energy band problem (Korringa 1947, Kohn and Rostoker 1954), we have followed the formalism of Onodera and Okasaki (1966). The trial wavefunctions in the interior of the spheres consists of an expansion in terms of the bi-spinors of the Dirac central-field problem (Rose 1961, Nazareno 1980):

$$[\alpha p + \beta mc^2 + V(r)]\psi_{\kappa,\mu}(r) = W\psi_{\kappa,\mu}(r) \quad (1)$$

these Dirac orbitals being

$$\psi_{\kappa,\mu}(r) = \begin{pmatrix} f_{\kappa}(r)\chi_{\kappa}^{\mu} \\ ig_{\kappa}(r)\chi_{-\kappa}^{\mu} \end{pmatrix} \quad (2)$$

where χ_{κ} are the eigenfunctions of J^2 and J_z .

Next we form the crystal wavefunction corresponding to a point k in the Brillouin zone superimposing the Dirac solutions. We have solved the secular KKR problem for each irreducible representation of the double groups of the wavevectors (Onodera and Okasaki 1966).

In this way our trial wavefunctions at the k -point in the Brillouin zone belonging to the α th irreducible representation is

$$\langle r|k, \alpha \rangle = \sum_{\kappa,\mu} C_{\kappa\mu}^{\alpha}(k)\psi_{\kappa,\mu}(r).$$

Faced with the problem of minimising the secular determinant in obtaining the

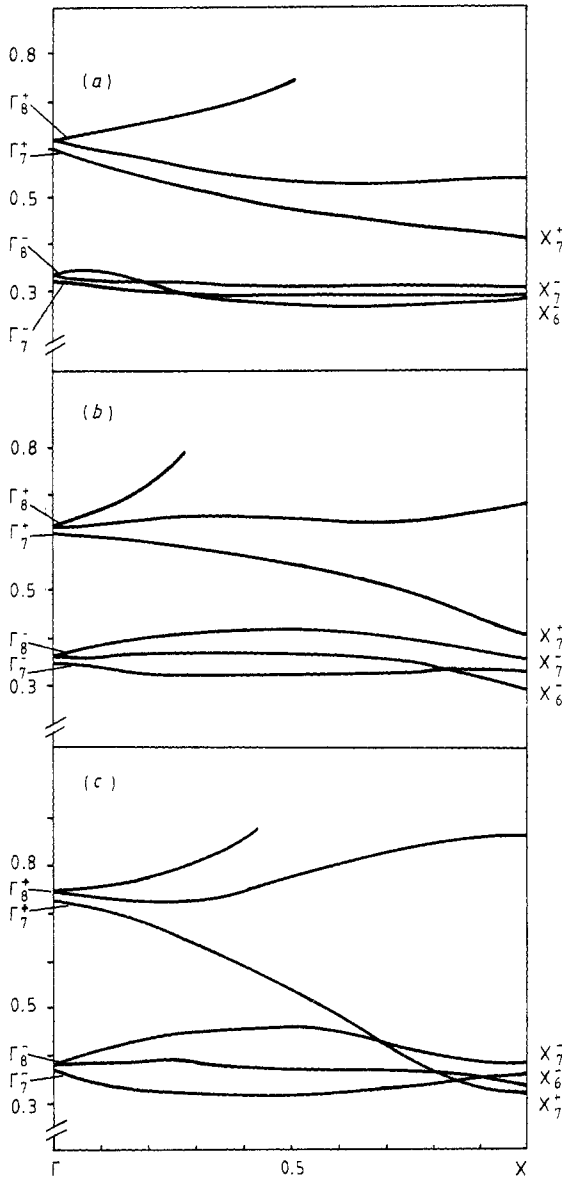


Figure 2. KKR energy band for SmSe in the Γ -X direction for $1.0V_0$, $0.90V_0$ and $0.80V_0$.

3. Discussion of the results

Our calculations indicate that in the present study of SmSe there is also an increase in the f band width Δ as the d band hybridises with the f bands. If we identify the inverse of Δ in the homogeneous mixed valence systems with the so-called valence fluctuation time or interconfiguration fluctuation time τ_{vf} , we note that an increase in Δ suggests reduced values of τ_{vf} . Experiments such as XPS which probe the sample on a time scale much shorter than τ_{vf} will see both configurations but experiments which probe on a

time scale longer than τ_{vf} will see only an intermediate configuration. When the effects of hybridisation on the Falicov–Kimball (1969) virtual bound-state model investigated by Iglesias-Sicard *et al* (1975) are included, it has been shown that there is a jump in Δ that gives rise to a transition from the phase of integral to intermediate valence.

As the volume is subsequently decreased, the d bands tend to pass through the f levels. Band crossing is not allowed and so the d bands hybridise with the f levels. The levels that are f type in much of the Brillouin zone become d like in a small region of the zone. At Γ , X and L, these bands have the opposite parity and thus cannot hybridise, giving rise to a metallic state. Along the Λ and Δ directions these bands have different symmetries over a certain range of k -values which because of the effect of pressure can effectively cross, leading to a metallic state. We note in figure 2 that at $0.80V_0$ the bottom of the conduction band at the zone edge X_7^+ has become lowered to a position below the f band, characterising the collapsed metallic phase. An investigation (Robinson 1979) of the physical properties of SmSe indicated that the compound undergoes valence changes at room temperature at a critical pressure and consequent volume change $\delta V/V$ of 0.13. This is qualitatively in agreement with the $\delta V/V$ -value about 0.15 obtained in this work. Our estimated values of $\delta V/V$ for SmS and SmTe are also within the reported range of experimental values.

From the energy bands in the Sm monochalcogenides it is clear that the density of states in the semiconducting phase has a strong peak in the narrow f bands which would suggest that on transition to the metallic phase these bands make an important contribution to the specific heat, since they are located in the neighbourhood of the Fermi energy in the metallic collapsed phase. For the semiconducting phase on the contrary, we would have, because of the large number of states involved, strong absorption caused by the f transitions from valence band to conduction band, i.e. $f(X_7^-) \rightarrow d(X_7^+)$, $f(\Gamma_8^-) \rightarrow d(L_6^+)$, $f(L_6^-) \rightarrow d(L_6^+)$ and $f(\Gamma_8^-) \rightarrow d(\Gamma_7^+)$. We note that the theoretical estimate of these transitions in SmS for which we also have the optical reflection spectra data obtained by Battlog *et al* (1976) and Zhuze *et al* (1978) yields good agreement between the four aforementioned transitions and the experimental peaks at 1.7 and 3.0–5.0 eV. Our calculations thus suggest that these peaks may be associated with electron transitions from the f band to the d-type states of the conduction band which is qualitatively in agreement with the work of Shuze *et al* (1978), which associates these two peaks with the electronic transitions $4f^6 \rightarrow 4f^5(^6H_7)5d(t_{2g})$ and $4f^5(^6F_7)5d(t_{2g})$.

Konczykowski *et al* (1985) have used a bound magnetic polaron acceptor model for SmS to indicate that the Fermi level is close to the $4f^6$ shell in the semiconductor phase below 3 kbar in SmS (Nazareno *et al* 1983). This is in agreement with our calculations for SmS which also yields similar results for SmTe (Caldas *et al* 1986) and SmSe as well.

Konczykowski *et al* (1985) also concluded that the observed semiconductor-to-metal transition above 4 kbar in the black phase of SmS is due to the overlap of the 5d conduction band with the $4f^6$ level which is also in agreement with our calculations for the Sm monochalcogenides. These workers have raised the question, however, of why the lattice collapse does not occur at 4 kbar but at higher pressures. Our calculations for the Sm monochalcogenides indicate that the reduction in the band gap is very sensitive to the reduction in the lattice parameter. A simple explanation would suggest that only above 4 kbar is the reduction in lattice parameter sufficient to reduce the small SmS band gap to zero. The different experimental values of band gaps for the Sm monochalcogenides would thus suggest that it would require different pressures to induce the semiconductor-to-metal phase transition in these Sm compounds; this is confirmed by experiment.

We would also like to comment on an important feature of our fully relativistic band structure for SmS, SmTe and SmSe, namely the location of the f bands, which was not dependent on adjusting exchange potential parameters, and also the accommodation of the six f electrons in the six available band states which arose naturally when the degeneracy of the double-group states is considered.

Clearly, to understand fully the properties of complex rare-earth systems and to obtain quantitative agreement between experiment and theory, detailed knowledge of the electronic structure is essential. In this respect, band theory has an advantage over experiment in that it can be used to examine the region that is inaccessible to experiment owing to the volume collapse. On the contrary, present-day band theory describes a single ground state only and only cannot describe the fluctuations.

4. Conclusions

As previously emphasised (Nazareno *et al* 1983), we suggest that relativistic effects such as spin-orbit coupling, and mass-velocity and Darwin corrections should be considered in calculating the band structure of rare-earth systems although other effects such as modification of the electronic structure and exchange potential, many-body corrections and multiplet structure of excited configurations may also effect these results. We are also aware of the importance of a self-consistent calculation when dealing with the electronic structure of f-electron systems. Such a calculation was done for SmS (Strange 1984) using the local-density-functional model and these bands show a general resemblance to those found in our previous KKR relativistic band calculations in SmS. In the Sm monochalcogenides, we find that the narrow bands arising from the atomic $J = \frac{5}{2}$ and $J = \frac{7}{2}$ levels are located near the Fermi energy. The self-consistency should not substantially alter our results, provided that we start with a charge density close to the correct value.

We note that the semiconductor-to-metal transition in SmSe as well as SmTe is continuous whereas it is discontinuous in SmS. If in these compounds the crystal structure is isostructural with the semiconducting rock-salt structure, the reduction in band gap with pressure per concomitant reduction in lattice constant has the same values as the deformation potential and then the transition will be smooth and continuous. If the misfit becomes too large as in SmS with a very small band gap, then the lattice adjusts discontinuously in a first-order transition (Battlog *et al* 1976). Our calculations suggest that the necessary pressure for reduction in band gaps per concomitant reduction in lattice constant required to induce the semiconductor-to-metal phase transition should be sensitive to the variations in experimental band gaps at atmospheric pressure in the Sm monochalcogenides.

Although the present band theory describes a single ground state only and cannot describe the fluctuations, we may nevertheless conclude on the basis of our fully relativistic KKR calculations for the samarium monochalcogenides that the present-day band theoretical models may give some sort of average behaviour in the collapsed state.

References

- Allen J W, Martin R M, Battlog B and Wachter P 1979 *Appl. Phys.* **49** 2078
Battlog B, Kaldis E, Schelegel A and Wachter P 1976 *Phys. Rev. B* **14** 5503

- Caldas A, Taft C A and Nazareno H N 1986 *J. Phys. C: Solid State Phys.* **19** 3615
- Davis H L 1977 *Rare Earths and Actinides 1977* (Inst. Phys. Conf. Ser. 37) p 126
- Falicov L M and Kemball J C 1969 *Phys. Rev. Lett.* **22** 997
- Iglesias-Sacardi J, Battacharjee A K, Julien R and Coqblin B 1975 *Solid State Commun.* **16** 499
- Jayaraman A, Narayammamurti V, Bucher E and Mainer R G 1970 *Phys. Rev. Lett.* **25** 1430
- Jefferson J H and Stevens K W H 1978 *J. Phys. C: Solid State Phys.* **11** 3919-47
- Kohn W and Rostoker N 1954 *Phys. Rev.* **94** 1111
- Konczykowski M, Bordie R G and Morello J 1985 *J. Magn. Magn. Mater.* **52** 437
- Korringa J 1947 *Physica* **13** 392
- Kuramoto Y and Müller-Hartmann E 1981 *Valence Fluctuations in Solids* ed L M Falicov, W Hanke and M P Maple (Amsterdam: North-Holland) p 139
- Lawrence J M, Riseborough P S and Parks R D 1981 *Rep. Prog. Phys.* 441
- Martin R M and Allen J W 1979 *J. Appl. Phys.* **50** 7561
- Nazareno H N 1980 *Solid State Commun.* **36** 301
- Nazareno H N, Caldas A and Taft C A 1983 *J. Phys. C: Solid State Phys.* **16** 887
- Onodera Y and Okasaki M 1966 *J. Phys. Soc. Japan* **21** 1273
- Ramirez R, Falicov L M and Kimball J C 1970 *Phys. Rev. B* **2** 3383
- Robinson J M 1979 *Phys. Rep.* **51** 1
- Rose M E 1961 *Relativistic Electron Theory* (New York: Wiley)
- Strange P 1984 *J. Phys. C: Solid State Phys.* **17** 4723
- Varma C M 1976 *Rev. Mod. Phys.* **48** 219
- Zhuze V P, Karin M G, Sidarin K K, Startsev G P and Shelykh A I 1978 *Fiz. Tverd. Tela.* **20** 3049