A Cluster-Like Approach for the Valence Transition in SmS Compounds

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The extended Falicov-Kimball model is applied to a cluster composed of three spinless ions. By one of these ions we simulate an interstitial impurity situation which often occurs in semiconducting SmS. The remaining two ions are taken as next nearest neighbours sitting on regular Sm lattice sites. For a proper choice of parameters these two ions may undergo a valence transition due to the presence of the impurity. The situation corresponding to an anionic impurity can be simulated in a similar way.

I. The Cluster Model

The resistivity measurements for irradiated SmS compounds can be interpreted by the presence of Sm self-interstitial at a tetrahedral position [1]. An appropriate theoretical approach which allows for a local valence transition (for example Sm$^{2+} \rightarrow$Sm$^{3+}$) at the sites being nearest neighbours of the interstitial impurity has been developed in [2, 3, 4]. Such a local valence transition can also be induced in the neighbourhood of an anionic point defect; i.e. S being substituted for example by O, As, P,... . This problem has been tackled theoretically, too [3, 5]. A list of experimental papers can be found in [5]. In Ref. [1–5] the semiconducting phase of SmS was considered for the case of sufficiently small enough impurity concentration in order to remain below the percolation threshold at which the intermediate valence transition takes place. For a recent review in this context we refer to [6].

The aim of the present note is to propose a simple model which allows for a simulation of the above mentioned effects in connection with interstitial impurities. A model consisting of a finite number of atoms has been considered in [4]. Here, however, we want to present a simplified version which makes the effect of a valence transition due to impurities more transparent. The model essentially consists of a cluster-like version of the extended spinless Falicov-Kimball Hamiltonian [7]. This Hamiltonian has earlier been used for a description of pressure induced valence changes [8].

In SmS each interstitial Sm ion is surrounded by four Sm nearest neighbours. The qualitative features of this situation can be described in a simplified manner by a cluster of five ions (see Fig. 1). One of them stands for the interstitial Sm ion, the other four ions of the cluster are two pairs of next nearest Sm ions. As a further simplification we simulate each of the two pairs by one effective Sm ion which of course is electronically different from the interstitial one [3]. We are thus led to the following model Hamiltonian:

$$H = \sum_{i=0}^{2} \left( \varepsilon_i n_i^d + E_i n_i^f + V_i (f_i^+ d_i + \text{h.c.}) + G_i n_i^d n_i^f \right) + \sum_{j \neq 0} t_{ij} d_i^+ d_j.$$  

(1)

Here, the first two terms describe the atomic d and f levels, respectively. $V_i$ stands for the intraatomic f–d hybridization and $G_i$ represents the intrasite Coulomb repulsion between d and f electrons. The last term allows for a hopping of d electrons. It is reasonable to assume $\varepsilon_1 = \varepsilon_2 = \varepsilon$, $E_1 = E_2 = E$, $V_1 = V_2 = V$, $G_1 = G_2 = G$, $t_{12} = t_{21} = t$, $t_{01} = t_{02} = t_{20} = t_0$, due to the fact that the two effective surrounding ions are identical. In the occupation number representation we are dealing with $2^6$ states (each $d$ or $f$
state can be empty or occupied within our spinless model. A linear combination of 20 of these states forms the ground state for the case of one electron per atom. The resulting eigenvalue problem is then solved by diagonalizing a \((20 \times 20)\)-matrix. This has been achieved numerically. From the coefficients of the ground state vector the different occupation numbers can then be calculated. The procedure is quite obvious and therefore we will not go into more technical details. For the same reason we have not written down the \((20 \times 20)\)-matrix. Only the results of the numerical investigations are presented.

II. Results

The average number of \(f\) electrons for both kinds of ions is presented in Fig. 2. For small value of \(V\) and \(V_0\) we obtain the integral valence case. If in addition the difference between the \(f\) levels \(E\) and \(E_0\) is large enough the valence of the interstitial atom is close to +2 and that of its neighbours close to +3 (Curves 1 and 2 in Fig. 2). Here, \(E_0\) is taken as \(E_0=0\). For larger values of \(V\) and \(V_0\) deviations from integral occupation numbers occur. This corresponds to the intermediate valence situation. The behaviour of the ground state energy as a function of \(E\) is also shown in Fig. 2. The situation of an anionic impurity can also be described with the help of the model Hamiltonian in Eq. (1). For example, a substitution of S by P in SmS will mainly influence the six nearest Sm ions of the original S lattice site and will eventually induce a valence transition. If we now group these six nearest Sm neighbours in 3 pairs of ions a situation is obtained which may be described by the model Hamiltonian if in addition all energy parameters for the three \textit{effective} ions are taken to be the same. The main effect of such an anionic impurity will consist in a shift of the energy of \(d\)-orbitals, e.g. \(\epsilon\), and in a change of the \(d\)-transfer integral between Sm ions. It is therefore interesting to see how \(\langle n^f \rangle\) changes as a function of \(\epsilon\). This is shown in Fig. 3. It is obvious from the figure that also in the case of an anionic impurity a valence transition can occur.

The valence transition in semiconducting rare earth compounds due to the presence of either interstitial or anionic impurities has been discussed by various authors [2–5]. Using different methods they also obtained for appropriate parameter values local valence transitions of rare earth ions occupying regular lattice sites. Thus, our results confirm those derived in [2–5] and are complementary to them.

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