Mechanism of valence transitions in rare-earth metal compounds

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In the case of strong coupling of f-d excitons with the lattice, their dipole-dipole interaction with each other produces a valence jump; otherwise, it smooths out the valence transition.

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As is known, the intermediate-valence states (IVS) in Sm compounds appear as a result of crossing of the $4f^6$ level in which the $6s$-$5d$-type conduction band (c band) is initially empty. There has recently been convincing experimental[1,2] and theoretical[3,4] evidence of strong, excitonic correlation between the f holes and the c electrons in the IVS. A valence transition from the semiconducting (B) phase of Sm chalcogenides to the IVS can, in principle, be an ordinary condensation or a Bose condensation of f-d excitons. Both types of transitions were discussed many times in connection with Mott excitons in semiconductors (see Ref. 5 and the references cited therein). In this case, however, a similarity between the absorption spectra of B phases in the excitonic region and the spectra of isolated Sm^{2+} ions[1] indicates that the exciton radius is small. This is consistent with a high (~ 0.6 per site) exciton density in the IVS. The band structure of dipole-active Frenkel excitons is determined primarily by their dipole-dipole interaction with each other. If the delocalization of c electrons (according to the estimates,[2] only $\sim 10\%$ of the delocalized c states lie below the $4f^5\,5d$ excitonic level) is completely disregarded, we can write the Hamiltonian of the system interacting f-d excitons in the form

$$H = \sum_i \left[E_{0i}(X)\,(1 - b_i^+ b_i) + E_{1i}(X)\, b_i^+ b_i \right] + \sum_{ij} W_{ij}(X)\,(b_i + b_i^+)(b_j + b_j^+), \qquad (1)$$

where b_i is the Pauli operator which annihilates the f-d exciton at the lattice site i (for simplicity, we disregard here the exciton polarization; see, however, the footnote[2]); E_{0i} and E_{1i} are the energies of the $4f^6$ and $4f^5\,5d$ levels, respectively, of an Sm^{2+} ion; W is the matrix element of the dipole-dipole interaction and X is a set of phonon coordinates. At $W=0$ the interaction of excitons with uniform deformations gives rise to a spasmodic valence transition with a variation of the number of $b_i^+ b_i$ by a unity, whereas the local polaron effects, which are important because of strong exciton-lattice interaction in the compounds under consideration, smooth out the transition (Ref. 6).[1)] On the other hand, if only the uniform deformations are taken into account, then the inclusion of the dipole-dipole interaction will also smooth out

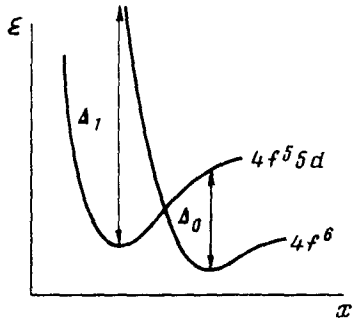

FIG. 1. $4f^6$ and $4f^5\ 5d$ levels of an Sm^{2+} ion; x is the normal coordinate of the totally symmetric oscillations of chalcogen ions.

the transition and stabilize the coherent IVS with $\langle b\rangle \neq 0$.[2] The result discussed below shows that allowance for the local polaron effects fundamentally changes the conclusions[2]: the dipole-dipole interaction primarily accelerates the transition and necessarily leads to a first-order transition such as the ordinary (not Bose-Einstein) exciton condensation at low temperatures.

To select the effects of interest to us, we shall examine only the local deformations, which correspond to totally symmetric oscillations of chalcogen ions relative to the Sm ions, and describe them in terms of the Einstein model (the role of the interaction between the modes is briefly mentioned below). Thus, $E_{0i} = \varepsilon_0(x_i, P)$ and $E_{1i} = \varepsilon_1(x_i, P)$ in Eq. (1), where ε_0 and ε_1 are the $4f^6$ and $4f^5\ 5d$ levels (Fig. 1), x_1 is the corresponding normal coordinate, and P is the pressure. The vertical gap between the ground state of the $f^6(f^5\ 5d)$ level and the $f^5 d(f^6)$ level is denoted by $\Delta_0(\Delta_1)$; $\Delta_1 \gtrsim \Delta_0$ because of anharmonism of the highly excited, vibrational states. At $W=0$ the system of clothed excitons is characterized by wave functions of the type

$$\prod_i \left[(1 - N_i)\ \phi_0(x_i) + N_i\ \phi_1(x_i)\, b_i^+ \right] |\ 0\rangle, \tag{2}$$

where N_i is the number of clothed excitons having the values of 0 and 1, ϕ_0 and ϕ_1 are the wave functions of the ground states of $4f^6$ and $4f^5\ 5d$ levels, and $|0\rangle$ is a state without excitons; the interaction with the lattice in this case shifts the transition point without changing its nature. We shall extimate the correction $E^{(1)}$ for the energy of state (2) due to dipole-dipole interaction. Assuming that the vibrational frequency $\omega << \Delta_0/h$, we obtain, as usual, a polaron band narrowing[8]: the matrix element of the dipole moment for the nonvertical transition between the main vibrational states of both levels is proportional to the small multiplier e^{-q}, where $q \sim \Delta_0/\hbar\omega$ is the average number of phonons produced as a result of the vertical transition. If

$$W << \Delta_0 << \Delta e^{2q}, \tag{3}$$

where Δ is the exact difference in energies of the ground states of the levels, then the dipole-dipole interaction can be calculated from perturbation theory and $E^{(1)}$ is determined primarily by the virtual vertical transitions. In the first nonvanishing order,

$$E^{(1)} = A + B \sum_i N_i + \sum_{ij} V_{ij} N_i N_i, \tag{4}$$

where A and B are unessential constants,

$$V_{ij} = -\frac{(\Delta_0 - \Delta_1)^2}{2\Delta_0 \Delta_1 (\Delta_0 + \Delta_1)} |W_{ij}|^2 \tag{5}$$

is the effective interaction of excitons. Since $V_{ij} < 0$, the nonuniform systems with Sm^{2+} ions in different states breaks up into two uniform phases at zero temperature. The physical advantage of separation is the fact that a reduction of energy due to exchange of virtual photons between two Sm^{2+} ions depends on the state of these ions because of the difference in the energy denominators[2)] ($2\Delta_0$, $2\Delta_1$, $\Delta_0 + \Delta_1$ for the $f^6 - f^6$, $f^5d - f^5d$, and $f^6 - f^5d$ pairs).

By comparing the energy of the phases with $N_i = 0$ and $N_i = 1$, we can determine the point of the first-order phase transition between them

$$\Delta = -\sum_i V_{ij} \sim W^2 / \Delta_0.$$

Thus, the inequality (3) holds at the transition point if

$$e^{-q} << W / \Delta_0 << 1. \tag{6}$$

The investigated simple model describes the spasmodic transition of all the Sm^{2+} ions from the f^6 state to the f^5d state. To understand the SmS transition to the IVS qualitatively, in addition to the long-range ($\sim 1/R^6$) attraction (5), we must take into account the short-range repulsion of excitons due to interaction of the local vibrational modes.[6,9] An effective interaction of excitons can also be produced by a partial delocalization of c electrons; moreover, a direct exchange of d electrons facilitates exciton attraction and an s-d hybridization facilitates their repulsion.[10]

A relatively high critical temperature $T_c \sim 10^3$ K of the transition to SmS (Ref. 11), as compared with the ordinary van der Waals systems, is attributable to the small $\Delta_0 \approx 0.8$ eV compared with the typical energy of the first excited state of an isolated atom. Δ_0 increases as a result of transition from SmS to SmSe and later to SmTe and the dipole-dipole interaction weakens because of an increase of the lattice constant and of the dielectric susceptibility of anions. This accounts for the absence of a transition to SmSe and SmTe at $T \approx 300$ K (they have not been investigated at low temperature). We note that at $T \gtrsim \hbar\omega$ the e^q factor in Eq. (3) must be substituted for $e^{\Delta_0/T}$. Since $\Delta_0/T_c \gtrsim 5$, the inequality $e^{-\Delta_0/T} << W/\Delta_0 << 1$, which is analogous to (6) and which enables us to use the perturbation theory and disregard the virtual nonvertical transitions, holds for intermediate W in the region $T \leqslant T_c$.

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[1)] If the anharmonism is taken into account, then the interaction with the uniform deformations can also smear out the transition.[7]

[2)]The same result can be obtained for purely parabolic levels if the polarization of the excitonic state is qualitatively taken into account.

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