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Electronic Structure and Properties of Rare Earth and 3*d* Transition Metal Compounds

R. Dagys[1] and G.-J. Babonas

Semiconductor Physics Institute, Lithuanian Academy of Sciences, Goštauto 11, 2600 Vilnius, Lithuania

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Excitation energies of various electronic configurations in rare earth and 3*d* transition metal compounds are considered and related to the peculiarities of the observed electrical and optical properties. Intraionic excitations of 4*f*, 3*d* electrons to less localized *nl* states are shown to be equally important as interionic *d*–*d* or charge transfer transitions usually considered, and to be even more significant in compounds containing low valence metals. © 1994 Academic Press, Inc.

INTRODUCTION

The discovery of high T_c superconductors and the problem of Cu–O planes, playing an important role in superconductivity, have once again revived the question about the relation between the electronic structure and physical properties of transition metal (TM) compounds. Recently, there appeared a series of works (see (1–3) and references therein) which attempts to explain the peculiarities of electrical and spectroscopical properties in many 3*d* TM compounds in the framework of a simple ionic crystal model, considering the relative values of $d^N + d^N \rightarrow d^{N-1} + d^{N+1}$, $d^N \rightarrow d^{N+1}\overline{L}$, $d^N \rightarrow d^{N-1}nl$, and $d^N nl\overline{L}$ excitation energies and corresponding bandwidths (here d^N denotes the ground electronic configuration of cation outer electrons, $\overline{L}$ is a hole in the valence *p* band, and *nl* specifies the cation electron state which is less localized than that of 3*d* electrons). In these investigations attention was paid mainly to intraionic $d \rightarrow d$ and charge-transfer $p \rightarrow d$ excitations, being the most important ones, with the corresponding energies U and Δ, which in a simple ionic model are expressed as $U = I_d(d^N) - A_d(d^N)$ and $\Delta = I_p(p^6) + |eV_M(p^6)| - [A_d(d^N) - |eV_M(d^N)|]$ (where $I_d(d^N)$ and $I_p(p^6)$ are ionization potentials of cation and anion, respectively, A_d is the electron affinity, and $V_M(d^N)$ and $V_M(p^6)$ are Madelung potentials at cation and anion sites, respectively). Regarding the values of U, Δ, and bandwidths W, which for simplicity were assumed to be the same for each state, these compounds were classified (1) as charge-transfer insulators ($W < \Delta < U$), Mott–Hubbard insulators ($W < U < \Delta$), *p*-type metals ($U > \Delta$, $\delta < W$), and *d*-type metals ($\Delta > U$, $U < W$). The U and Δ values were calculated (3) for a large number of TM and rare earth (RE) oxides using the free ion ionization potentials. According to U and Δ values, these oxides were shown to be divided into three groups: insulators with large values of $U \approx \Delta$ and two groups of metals with $U < \Delta$ and $U > \Delta$. The results obtained were interpreted as an indication in favor of validity of this simple classification.

Less attention was paid to intraionic 3*d*–*nl* and interionic *p*–*nl* excitations, assuming that their energies were rather large, and, hence, they were of minor importance in determining the peculiarities of properties in TM compounds (4). However, this statement has been grounded on the data of free ions. For ions in crystals the energies of d^N–$d^{N-1}nl$ excitations may be significantly reduced with respect to those of free ions. As proper examples, one can consider the well-known peak at 4.1 eV in the optical spectra of the $YBa_2Cu_3O_6$ compound, which has been intensively studied previously (5), and the optical feature which is observed in A_2CuX_3 (A = K, Rb; X = Cl, Br) (6) at the energy (4.5 eV) is only slightly dependent on substitution of elements *A* or *X*. Both of these optical features are attributed to the 3*d*–4*p* transitions of Cu^+ and reveal themselves at energies which are smaller by a factor of two than the energy of the lowest 3*d*–4*p* excitation in free Cu^+ ion (8.2 eV (7)).

One of the important results of such a large decrease of the 3*d*–*nl* excitation energy is that it can be an additional screening of potential for electrons of metal ion in crystal due to overlap of their functions with electrons of ligands. In a pure ionic crystal model such screening is neglected, assuming that in the region of the metal ion the Madelung potential, representing the spherical part of potential of the rest of the crystal, is constant. The role of this screening on the 3*d*–*nl* excitation energies may be roughly estimated using the Slater model of overlapping neutral atoms (8), i.e., taking into account that, for example, in NiO or

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[1] To whom correspondence should be addressed.

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EuO an appreciable transfer of outer 4*s* or 6*s* electrons onto oxygen atoms does not occur because the maximum charge density of these electrons in crystal is approximately at the same place as that of 2*p* electrons in neutral O atoms. Therefore, this screening can be simply accounted for in crystal using 3*d*–*nl* excitation energies of neutral atoms.

Regarding monovalent Cu ions in crystals, a more realistic approximation is to compare the energy of 3*d*–4*p* excitation with that of $3d^{10}4s$–$3d^94p4s$ excitation in neutral atoms, the latter being equal to 5.0 eV (7) for the ground states. Taking into account the crystal field splitting of $3d^9$ states, this value is very close to that of the energies of the corresponding peaks in the optical spectra of crystals mentioned above.

It is reasonable to assume that this screening is responsible for a decrease of the Slater parameters $F^k(dd)$ for ions in crystals, because the values of $F^k(dd)$ for $3d^N$ ions in crystals as well as for $3d^N4s^2$ neutral free atoms are 10–20% lower than those for free $3d^N$ ions. Additionally, in both cases the decrease shows the same tendency when passing from the left to right of the $3d^N$ series. For example, the empirical values of $F^2(3d3d)$ for $3d^3V^{2+}$ and $3d^8Ni^{2+}$ are equal to 7.2 and 10.5 eV, respectively, while for the corresponding neutral atoms in $3d^N4s^2$ configuration they are equal to 5.6 and 9.7 eV.

In the present paper we show that intra-atomic *d*–*nl* and interatomic *p*–*nl* excitations are as important as interatomic *d*–*d* or charge-transfer *p*–*d* transitions for the interpretation of the physical properties of crystals, particularly of those with the low formal valency of metals. Along with TM compounds, the RE materials are considered for several reasons. First, the problem of the relationship between the electronic structure and physical properties is similar for compounds of both groups. Second, there are many empirical data for a great number of RE compounds with the same crystal structure but different anions and cations, as well as a great body of information which is concerned with excited states of free RE ions and ions in crystals, and which is suitable to check various theoretical models. Third, the role of such effects as a strong crystal field, covalency, and mixing of the d^N,d^{N-1},$d^{N-2}s^2$ configurations of the same parity, which are rather difficult to be estimated in TM compounds, is less important in RE materials due to a strong localization of 4*f* electrons.

RE COMPOUNDS

The well-investigated RE monoxides and monochalcogenides *LnX* (*Ln* = RE element and *X* = O, S, Se, or Te) represent a simple example which shows that, in general, divalent metal ion compounds cannot be attributed in advance to the group of low *U* metals. According to (3), they fall into the group of compounds with $U < \Delta$. However, considering only the interionic *f*–*f* excitations (see *U* values for Ln^{2+} ions in Table 1) it is impossible to explain the fact that only compounds with *Ln* = Sm, Eu, Tm, or Yb are insulators (9) among *LnX* crystals with the same NaCl-type structure.

On the other hand, the distinctive features of these four elements are the largest ionization energies of 4*f* electrons, the largest intervals $E_{4f}^{5d}(Ln^{2+})$ between the ground states of the ground $4f^N$, and the first excited $4f^{N-1}5d$ configurations connected with them. According to the comment made above, let us consider $E_{4f}^{5d}(Ln)$ for neutral atoms instead of $E_{4f}^{5d}(Ln^{2+})$ for Ln^{2+} ions. As it is seen from experimental data (10) presented in Table 1, the values of $E_{4f}^{5d}(Ln)$ for *Ln*, corresponding to metallic *LnX* compounds, are smaller than 1 eV and may also be smaller than the bandwidth $W \approx 1$ eV (11) of 5*d* states, taking into account the typical values of 1–3 eV (9) for the crystal field splitting of 5*d* electrons. For Eu and Yb, which have the largest values of E_{4f}^{5d} for free *Ln* atoms, in crystal the inequalities $E_{4f}^{5d} > W$ are valid for all *X*, and the corresponding compounds are insulators. For Sm and Tm, which have E_{4f}^{5d} values smaller than those for Yb or Eu, the previous condition is valid only for heavier *X*, in which the crystal field splittings are smaller. Because of this reason, for the Sm*X* group only SmS, SmSe, and SmTe are insulators, whereas for Tm, which has the smallest value of E_{4f}^{5d} among these four elements, only TmTe is an insulator. Since the ionic radius in the $4f^{N-1}5d$ configuration is smaller than that in $4f^N$, a lattice constant for metallic *LnX* is expected to be also smaller than that in the case of the corresponding insulating *LnX* compound. This is in good agreement with experimental data (9).

Thus, the peculiarities of electrical properties of *LnX* compounds can be explicitly interpreted considering the relative location of the energy levels of atomic 4*f* and $4f^{N-1}5d$ configurations in crystals.

The $4f^N$–$4f^{N-1}5d$ excitations are also responsible for absorption edge E_g of insulating *LnX*. This conclusion is based, at first, on a typical red shift of E_g in a series of Te–Se–S–O compounds (9, 11), which is due to an increase of the crystal field splitting of 5d levels. Second, there is a good correlation between E_g in *LnX* and the energies of the lowest $4f^N6s^2$–$4f^{N-1}5d6s^2$ transitions in the corresponding free *Ln* atoms. Moreover, in a well-investigated Eu*X*, the energy of the center of gravity for 4*f*–5*d* transitions, which equals 3.1 eV for different *X* (12), is in reasonably good agreement with the value of $E_{4f}^{5d} = 3.4$ eV (10) for the neutral Eu atom.

More intense features manifest themselves in the optical spectra of Eu*X* at energies 1–3 eV above E_g (12). The latter blue shift determined in a series of Te–Se–S–O compounds correlates well with ionization energies of *p* electrons of the corresponding *X* atoms. In contrast, the

TABLE 1

The Values (in eV) of Parameters U for Ln^{2+} Ions and the Intervals (in eV) $E_{4f}^{5d}(Ln^{2+})$ and $E_{4f}^{5d}(Ln)$ between the Ground States of Configurations $4f^N$ and $4f^{N-1}5d$ for Ln^{2+} Ions and Configurations $4f^N6s^2$ and $4f^{N-1}5d6s^2$ for Neutral Ln Atoms, Respectively (10)

	Pr	Nd	Sm	Eu	Tb	Dy	Ho	Er	Tm	Yb
U	15.6	15.8	14.6	22.7	16.4	18.4	18.8	17.3	16.8	14.5
$E_{4f}^{5d}(Ln^{2+})$	1.59	1.89	3.26	4.20	1.11	—	2.23	2.10	2.84	4.14
$E_{4f}^{5d}(Ln)$	0.55	0.84	2.24	3.42	0.04	0.94	1.04	0.89	1.63	2.87

energies of these optical features are weakly dependent on Ln. Therefore, the features are to be attributed to p–nl rather than to the charge-transfer p–$4f$ transitions. In the latter case a strong dependence of transition energies on Ln should be determined because electron affinities $A_{4f}(Ln^{2+})$ for divalent ions differ significantly and are equal to 8.8, 2.1, 6.9, and 10.5 eV (10) for Sm, Eu, Tm, and Yb, respectively.

Thus, the peculiarities of optical spectra of insulating RE compounds with divalent cations may be simply interpreted in the single configurational approximation. For the most part, this simplicity is due to the specificity of the $4f^N$ states.

With an increase in the valence of metallic atoms, the role of different types of excitations in determining the physical properties of RE and TM compounds is essentially changed. First, the energies of $3d$,$4f$–nl excitations are increasing and, hence, the corresponding transitions are less important in the vicinity of the absorption edge. Second, the values of the U parameter for both RE and $3d$ TM elements slightly depend on the ionization degree. Third, the values of $I_p(p^6) + |eV_M(p^6)|$ for various compounds with the same p^6 anions are close together and are approximately equal to ionization potentials of p electrons in the corresponding free neutral atoms (3). In addition, with an increase in the ionization degree, the value of $A_d(d^N)$ is increasing faster than $|eV_M(d^N)|$. As a result, according to definition, parameter Δ is smaller for metallic atoms with higher valency. Therefore, the charge-transfer transitions and p–nl excitations are expected to play a dominant role for compounds containing RE or TM ions in the states higher than divalent ones.

As an example of RE materials with higher valence of metallic atoms, let us consider Ln_2S_3 compounds whose optical and magneto-optical properties have been extensively investigated (13) for Ln = La, Ce, Pr, Nd, Gd, or Dy. The absorption edge of these sulfides ($E_g \approx 3$ eV) is weakly dependent on Ln and is smaller by approximately 2.5 eV than that of Ln_2O_3. Such a difference in E_g values for Ln_2S_3 and Ln_2O_3 agrees well with the difference in ionization potentials for p electrons in S and O. Therefore, the absorption edge must be formed by optical transitions from the p valence band. On the other hand, taking into account a weak dependence of E_g on Ln, the corresponding excited states are to be attributed to p^5f^Nnl rather than p^5f^{N+1} states, since in the latter case the state energy strongly depends on Ln (10). This result is in good agreement with the fact that all the LnX compounds with Ln = La, Ce, Pr, Nd, Gd, and Dy are metallic, since according to the model used above to explain the peculiarities of electrical properties of LnX, the f^Nnl states are located lower than f^{N+1} states in the corresponding Ln^{2+} ions in crystals.

The only exception to Ln_2S_3 compounds is Ce_2S_3. In the optical and magneto-optical spectra of Ce_2S_3 below E_g (at 2.2 eV (13)) there exists a rather strong feature, which is assigned to the $4f$–$5d$ transitions of Ce^{3+}. Thus, even in compounds with metals in a trivalent state, intraatomic transitions may be important in determining optical properties. An appearance of the low energy feature for only Ce_2S_3 can be explained by the smallest energy of the $4f$–$5d$ excitation in Ce^{3+} among Ln^{3+} ions ($E_{4f}^{5d}(Ce^{3+}) = 6.2$ eV (10)) and in some sense is a manifestation of the Ce tendency to form a quadrivalent state in some compounds.

As follows from the case of Ce_2S_3, the decrease of E_{4f}^{5d} for trivalent RE ions in crystals with respect to the corresponding values for free ions is significantly larger than that for divalent RE ions. This larger decrease cannot be simply explained by an increase of the crystal field splitting or of the widths of $5dt_{2g}$ subbands in compounds with trivalent RE ions. As was shown in (14), the shift of E_{4f}^{5d} in Ce_2S_3 relative to that in $(La_{0.99}Ce_{0.01})_2S_3$, which reflects the influence of the $5d$–$5d$ overlap, is approximately equal to 0.3 eV. Thus, the width of the $5dt_{2g}$ subband in Ce_2S_3 is very similar to that in EuS (11). On the other hand, as follows from the spectra of the Ce^{3+} ions in various hosts (15), the shift of the $5dt_{2g}$ level due to the crystal field splitting does not exceed 1.5 eV. Therefore, it may be expected that the larger decrease of E_{4f}^{5d} for trivalent RE ions in crystals as compared with that for divalent RE ions is due to additional screening by a third "transferred" electron.

3*d* TM COMPOUNDS

The energies of the lowest $3d$–nl excitations in $3d$ TM free ions are higher than those of $4f$–nl excitations in RE ions of the same valence. Therefore, these excitations may be expected to play a less important role in determining the physical properties of $3d$ TM compounds. However, a significant decrease of these energies due to the screening of $4s$ electrons is to be taken into account. For example, E_{3d}^{4p} for $3d^N$–$3d^{N-1}4p$ excitations in M^+ and M^{2+} is higher by approximately 3 and 5 eV, respectively, than those for $3d^N4s$–$3d^{N-1}4p4s$ and $3d^N4s^2$–$3d^{N-1}4p4s^2$ excitations in the neutral M atom (7). Therefore, for ions in crystals the values of E_{3d}^{nl} may be rather small and may be comparable with the energies of the other excitations, particularly in compounds with metal atoms of lower valence.

In TM compounds attention was paid mainly to the investigations of TM monoxides MO. In the MO group, only TiO and VO are metals and fall into the region of $U < \Delta$, according to (3). This is, in principle, the main argument for regarding these compounds as metals of the Mott–Hubbard type, because another necessary condition $U < W$ is difficult to prove. However, the calculations performed on the basis of the free ion data and taking into account polarization effects have shown (2) that, for instance, the U value for V is larger than those for Cr and Fe, and is close to those for Co and Cu. Therefore, in the framework of the model used in (3) it is difficult to explain the fact that monoxides of these elements are also not metals. More probably, the origin of metallic properties of TiO and VO is the same as in metallic LnX and is due to the inversion of energy levels of $3d^N$ and $3d^{N-1}nl$ configurations of M^{2+} ions in crystals, as was suggested earlier by Koiller and Falicov (16).

Let us assume that, as in the case of Ln^{2+}, the interval E_{3d}^{nl} between the ground states of $3d^N$ and $3d^{N-1}nl(nl = 4s,4p)$ configurations for the M^{2+} ion decreases in crystal mainly due to the screening of "transferred" $4s^2$ electrons and to the formation of the nl-states band. Then one may expect that an inversion of $3d^N$ and $3d^{N-1}nl$ states is more probable in TiO and VO, in which both effects mentioned above are more important (17, 18). This is also because of a continuous decrease of $E_{3d}^{nl}(M^{2+})$, when passing from the right to left of the $3d$ series (7), with the exception of Mn^{2+} and Fe^{2+}, in which anomalies due to the strong exchange stabilization of ground terms of d^5 states occur.

Using the latter approximation, it can be clearly explained why the M–O distances in TiO and VO are shorter than those in the insulating MO compounds (as in the case of metallic and insulating LnX) and are approximately the same (3) as in oxides with trivalent cations Ti_2O_3 and V_2O_3. The assumption, that shorter M–O distances in TiO and VO are due to the absence of $3de_g$ electrons in Ti^{2+} and V^{2+} (2), is hard to accept. First, it is well known that the atomic radius is mainly determined by the spherical part of potential. Second, for example, for Ti^{2+} in cubic crystal field the ground state $t_{2g}^2\,{}^3T_1$ is strongly mixed with $T_{2g}e_g\,{}^3T_1$.

The problem of the origin of the optical gap E_g in insulating MO is more complicated than in LnX. For example, as is obvious from the free ion experimental data (7), the optical gap in monoxides MO (M = Mn, Co, or Ni) cannot be interpreted by a single type of excitation, in contrast to the case of LnX. Moreover, as was mentioned in (1), different types of excitations are expected to manifest themselves at close energies for an individual MO compounds. For example, in the region of 2–3 eV above E_g several optical features exhibiting different temperature dependences are observed (19, 20) and hence are to be attributed to different types of excitations. Therefore, the spectrum in the vicinity of E_g, obtained in a single configurational approximation, may be essentially changed by corrections of the order of 1–2 eV because of a mixing of configurations. Corrections of such an order are typical of $3d^N$ ions, as is clearly seen, for example, from comparison of the differences between ionization potentials $\Delta I_{3d} = I_{3d}(M_1^{2+}) - I_{3d}(M_2^{2+})$ and intervals $\Delta E_{3d}^{4s} = E_{3d}^{4s}(M_1^{2+}) - E_{3d}^{4s}(M_2^{2+})$ between the ground states of $3d^N$ and $3d^{N-1}4s$ configurations for two M_1^{2+} and M_2^{2+} ions. Since the energy of the $4s$ electron depends weakly on M, one can expect that $\Delta E_{3d}^{4s} \approx \Delta I_{3d}$ in the single configurational approximation. This equality is valid for the Ni–Cu pair, but $\Delta E_{3d}^{4s} - \Delta I_{3d} = 1.8$ eV (7) for a pair of Mn–Co. Therefore, the errors in the single configurational approximation may be rather large and are different for various M^{2+} ions.

Corrections of the same order of magnitude may be also expected because of a mixing of excited $3d^{N-1}4s$, p^53d^{N+1}, p^53d^N4s and $3d^{N-1}(\vec{R}_i)3d^{N+1}(\vec{R}_j)$ configurations. For example, the mixing between $3d^{N-1}4s$ and p^53d^N4s, or p^53d^{N+1} and $3d^{N-1}(\vec{R}_i)3d^{N+1}(\vec{R}_j)$ configurations is determined by the same matrix elements as those for covalent mixing which leads to corrections of order of 1–3 eV (21).

Thus, it is difficult to interpret the origin of the absorption edge and optical features near E_g of the insulating MO compounds in the framework of a single configurational approximation.

The problem of determining the origin of E_g may be expected to be simpler in the case of TM compounds with trivalent metal atoms, which fall into the group of insulators with $U \approx \Delta$ according to (3). In these compounds the E_g is most probably due to the charge-transfer transitions, taking into account the above-mentioned remarks concerning the dependence of various parameters on the valence of metallic atoms, and the fact that the energies E_{3d}^{nl} are larger than E_{4f}^{nl}. However, an absence of systematic investigations of TM compounds with the same crystal structure and different M and X makes this statement difficult to confirm directly from the optical data, as was done for Ln_2S_3. The available data obtained on individual crystals are insufficient because of the problem of separating the contributions to the spectra arising from the excitations of different types.

The charge transfer origin of E_g in these compounds can be confirmed by the results on well-studied magnetic insulators ACr_2X_4 (A = Cd, Hg; X = S, Se). On the basis of optical spectra for different A and X, and magneto-optical studies, which permit separation of p–$4s$ transitions from p–$3d$ ones,and by taking into account temperature dependences of the spectra, it has been shown (see (22) and references therein) that, as a matter of fact, the absorption edge in these compounds is due to the $p^6dt_{2g}^3$–$p^5dt_{2g}^3de_g$ transitions.

Finally, it should be noted that the metallic TM compounds, containing TM ions in tetravalent state and falling into the region $\Delta < U$ according to (3), in fact may be attributed to the p-type metals, taking into account an increasing role of the charge-transfer transitions with increasing valence of metal ions.

CONCLUSIONS

In the ionic model we have considered the relative arrangement of the ground levels of $n_0l_0^N$, $n_0l_0^{N-1}(\vec{R}_i)n_0l_0^{N+1}(\vec{R}_j)$, $\overline{L}n_0l_0^{N+1}$, $\overline{L}n_0l_0^Nnl$, and $n_0l_0^{N-1}nl(n_0l_0 = 3d, 4f)$ configurations and its relation to the electrical and optical properties of $3d$ TM and RE compounds. We have shown that the energies of intraionic $n_0l_0^N$–$n_0l_0^{N-1}nl$ excitations may be considerably smaller in crystals than those in free ions and that the physical properties of compounds containing metals with low formal valences depend mainly on a relative location of energy levels in these configurations. As an apparent confirmation of this assumption, the properties of the widely investigated RE chalcogenides could be considered. The properties of compounds containing higher valence metals are mainly determined by the charge-transfer excitations whose energies evidently decrease with increase of cation valences. For insulators with trivalent metals, this model agrees well with the experimental optical and magneto-optical data of a series of RE sesquisulfides and chromium spinels. Metallic compounds with formal quadrivalent metals may be attributed to the charge-transfer-type metals.

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