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Exchange-Perturbation Treatment of Magnetic Ordering in Nonconducting Solids

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Many nonconducting ionic solids with open-shell $3d$ or $4f$ cations exhibit magnetic order at low temperatures. In this paper such ordering is analyzed on the basis of exchange-perturbation theory applied to a complex of two paramagnetic cations and one diamagnetic anion in different geometric configurations. The perturbation energy is then summed over all complexes in the solid, for a given structure and for different spin patterns. The unperturbed Hamiltonian is chosen such that it is invariant under permutations of all electrons of the complex; the unperturbed ground-state wave function is an eigenfunction of this Hamiltonian. Full permutation symmetry is thus taken into account from the outset. On the other hand, space-group (or point-group) symmetry is not considered. An effective-electron model with four electrons on three centers is used to evaluate the influence of a diamagnetic anion on the interactions between unpaired electrons of two cations (superexchange). In addition, the effect of the valence shells of the cations on the cation-cation interaction is taken into account on the basis of a two-center six-electron model. The perturbation energies are evaluated in first and second orders, using Gaussian wave functions for the orbitals of the effective electrons. It is found that the model predicts both ferromagnetic and antiferromagnetic orderings, the type of ordering depending upon the extensions of the orbitals for the different effective electrons, the lattice parameters, and the symmetry of the crystal. It is established that exchange between unpaired electrons via the anion, when summed over the crystal, generally favors antiferromagnetic alignment of the spins, whereas indirect exchange via the cation valence shells leads to ferromagnetism. The model is applied to magnetic ordering in the Mn and Eu chalcogenides. Specifically, EuO and EuS are found to be ferromagnetic, whereas the remaining Eu salts are antiferromagnetic of the second kind. For the Mn compounds the indirect exchange via cation valence shells does not affect the stable magnetic structure, which is then determined by (antiferromagnetic) superexchange. Néel and Curie temperatures for the Mn and Eu chalcogenides calculated on the basis of this model are in fair agreement with experiment. A detailed calculation of the coupling parameters J_1 and J_2 for the systems MgO : V^{2+} and MgO : Mn^{2+} is made and the results are compared both with experiments and with recent configuration- interaction analyses. The observed positive (ferromagnetic) sign of J_1 in MgO : V^{2+} is reproduced by the model.

I. INTRODUCTION

The discovery[1] of ferromagnetism in solid EuO below 69.4 °K came as a surprise, since ionic solids with paramagnetic cations are usually found to be antiferromagnetic at the lowest temperatures, or to show a more complicated magnetic behavior. Later, ferromagnetism was also detected with EuS (Curie temperature $T_C = 16.5$ °K) and GdN ($T_C = 60$ °K), whereas EuSe is ferromagnetic below 2.8 °K and antiferromagnetic in the range 2.8–4.6 °K. EuTe is definitely antiferromagnetic. For a detailed account of the properties of the europium chalcogenides we refer to recent review articles.[2,3] As the solids of high purity are not electrical conductors, the ferromagnetic coupling at the lowest temperatures cannot be ascribed to indirect exchange via conduction electrons.

Insight into the possible explanation for the ferromagnetic behavior of some of the Eu salts can already be obtained[2] when we consider a reference anion in the lattice and its nearest-neighbor Eu cations. The solids of these salts have the NaCl ($B1$) structure composed of two interpenetrating face-centered-cubic lattices for the two types of ion. The coordination number of the $B1$ structure is six, i.e., a reference anion is surrounded by six nearest-neighbor Eu cations. The simplest possible model to describe magnetic properties then employs a ferromagnetic coupling parameter J_1 and an antiferromagnetic superexchange coupling J_2 via a diamagnetic anion. The observation that EuTe is antiferromagnetic means that J_1 varies more rapidly that J_2 in the series EuO, EuS, EuSe, and EuTe. For this reason one postulates that J_1 refers to a direct cation-cation interaction.

There are two well-known versions of a theory of superexchange, namely, Anderson's "potential- and kinetic-exchange method"[4] and the application of the configuration-interaction method by Keffer and Oguchi.[5] In the first method, the treatment of superexchange is divided into two steps: First, localized Hartree-Fock wave functions (Wannier functions) are constructed for a magnetic electron on one cation in the field of all anion ligands and of the other cations, but without considering exchange between magnetic electrons on different cations. In the second step, exchange between two magnetic electrons on different cations with wave functions as modified by the lattice is taken into account. If we assume one effective unpaired electron per cation, then this treatment of superexchange is reduced to that of evaluating the energy of a system of two one-electron atoms with electron wave functions distorted (polarized) by the ligands. In the second step of this procedure, therefore, the anions are no longer explicitly considered, and it is no longer possible to distinguish between direct exchange and indirect exchange (via the anions). Two types of exchange contribution to the energy of the system arise, which can be called "ionic" (or "nontransfer") and "transfer" exchange. The first is just a consequence of the Pauli principle applied to the system of two magnetic electrons on different cations; since Wannier functions at different centers are orthogonal, this contribution favors parallel alignment of the spins ("potential" exchange). The transfer-exchange terms are of the form $J=-b^2/2U$, where J denotes one-half of the energy difference between singlet (antiparallel) and triplet (parallel) alignments of the two spins, and where $U(>0)$ is the energy necessary to transfer a magnetic electron from one cation to the other; b is the corresponding transfer integral. This term, therefore, favors antiparallel alignment of the spins (so-called "kinetic" exchange).

In the application[5] of the configuration-interaction method to superexchange, on the other hand, a superexchange unit consisting of two cations and one anion is considered as a whole. Wave functions for this system which are eigenfunctions of S^2 and S_z are constructed as linear combinations of functions for the separate ions, with admixtures of excited states to allow for virtual electron transfer of different types between the ions. A variational calculation is then carried out to determine the energies for singlet and triplet states, taking initially one effective magnetic electron per cation and two spin-paired electrons for the anion (three-center four-electron system). This method has in recent years been extensively applied to different systems by Huang and Orbach.[6,7] In particular, they studied the effect of nonorthogonality of cation wave functions at neighboring sites in the lattice on the sign of the magnetic coupling between them. This effect was found to be important in the case of a 90° cation-anion-cation configuration of V^{2+} ions in a weak octahedral field (solid MgO). They also showed[7] that nonorthogonality of cation wave functions can lead to a reversal of the sign of the semiempirical Goodenough-Kanamori rules (see, e.g., Ref. 4).

Although the Anderson method and the configuration-interaction (CI) procedure have different starting points, the expressions obtained in an application to the same physical system are identical to the lowest order in overlap (in the CI sense) and transfer integrals. This has recently been demonstrated by Huang Liu and Orbach[7] in an application to the system of two V^{2+} ions in MgO. We will return to the results of the CI method, especially in relation with the sign of a 90° cation-anion-cation exchange, later on in this paper.

Detailed application to $4f$ compounds of the above treatments of superexchange developed for the interpretation of magnetic order in solids with $3d$ cations has, so far, not been made. Instead, a number of different mechanisms has been proposed in the literature to explain the observed ferromagnetism of EuO, EuS, and GdN and the transition to antiferromagnetic behavior for Eu chalcogenides with heavier anions. Such mechanisms are discussed in the review articles[2,3] referred to above; they are either based on a localized description or involve a hybrid model with localized unpaired electrons and a band model for the electrons responsible for the coupling. It appears, however, that the agreement with experiment is at best qualitative and that it is very difficult to reliably estimate the magnitudes of these effects. In addition, the effects often involve high orders of perturbation theory, so that the problem concerning convergence of the perturbation series may well be a serious one.

The present paper constitutes an attempt to explain magnetic ordering, and to evaluate transition temperatures, for nonconducting ionic solids with $3d$ and $4f$ open-shell cations *on the basis of the same simple model*. To describe this model, it is most convenient to adopt a perturbation analysis. As an unperturbed state of the system we can, in principle, consider that of the solid in which the ions interact only due to their net charges. The zeroth-order wave functions must be symmetry adapted to both the space group of the crystal and to the permutation group of the total number of electrons. Such a complete analysis is difficult to carry through; instead, we will in this paper restrict ourselves to the role of permutation symmetry in magnetic ordering. Since we are dealing with exchange interactions it seems to be a relevant condition on the model that full permutation symmetry be imposed from the outset. Instead of using, as is often done in the literature, only partially antisymmetrized wave functions, or of incorporating the effect of exchange through additional terms in the Hamiltonian, we thus start with a fully antisymmetrized wave function.

The analysis presented in this paper is based from the outset on a superexchange unit of two cations and one ligand anion, with full permutation symmetry of the unperturbed wave functions. Exchange-perturbation theory provides an appropriate simple tool for the evaluation of exchange interactions. Further, in neglecting translational symmetry we base ourselves on a localized instead of a band description.

The complex *MXM* consisting of two paramagnetic cations *M* and one diamagnetic anion *X*, in different geometric configurations, is taken as the fundamental unit for the evaluation of magnetic interactions and magnetic ordering. In a perturbation treatment, the total (spin-free) Hamiltonian H for this complex is written as the sum of an unperturbed part H_0 and a perturbation H'; the part H_0 refers to the isolated ions and H' comprises, as usual, interactions between electrons at different centers, interactions between electrons at one center and the nuclei of the other centers, and nucleus-nucleus interactions. The condition of full permutation symmetry of H_0 (and H') can be realized[8] by a redefinition (symmetrization) of these operators such that the antisymmetrized ground-state wave function is indeed an eigenfunction of the symmetrized H_0. A complete set of orthonormal antisymmetric functions can then be constructed by using the Schmidt orthogonalization procedure. These functions are, except the one describing the ground state, generally not eigenfunctions of H_0, although the diagonal elements of H_0 in this basis do correspond to a sequence of energy values for the unperturbed system. For details we refer to Ref. 8.

This procedure leads to a Rayleigh-Schrödinger type of exchange-perturbation theory. A consequence of the formalism is that the permutation symmetry of the Hamiltonian is *not* changed (increased) by adding the perturbation. Stevens[9] has recently pointed out that this condition may be an essential one in dealing with exchange in insulators by perturbation methods.

To evaluate the expression for the perturbation energy, we adopt the simplest possible model. First, we use the well-known three-center four-electron system for superexchange (one "effective" electron per cation, two spin-paired "effective" electrons per anion). In addition, we consider indirect interactions between paramagnetic electrons on two cations via their own closed outer shells. In our model, the closed outer shells of each cation are represented by two spin-paired effective electrons, so that the valence-shell indirect exchange is based on a two-center six-electron system. It has been suggested in the literature by several authors[10,11] that indirect exchange between unpaired localized electrons via filled valence bands must be considered for magnetic interactions. The present representation of this indirect exchange in terms of localized valence shells avoids using a hybrid version of such a mechanism.

Direct exchange between unpaired electrons is also taken into account, although its effect on magnetic stability is generally very small.

II. FORMALISM

We consider a complex *MXM* of two paramagnetic cations *M* and one diamagnetic anion *X*, in an arbitrary geometric configuration. The centers of the cations are denoted by a and c, the center of the anion by b. Further, let θ denote the opening angle at the site of the anion. The unpaired ($3d$ or $4f$) electrons of each cation are replaced by one effective electron, the anion shells by two spin-paired effective electrons. In addition, we replace the closed outer shells of each cation by two spin-paired effective electrons. Three types of interaction for the complex *MXM* are considered:

(a) *Direct exchange* between the unpaired electrons on the two cations. Here, the model is based on a two-center two-electron system.

(b) Indirect exchange between unpaired electrons on the two cations via the diamagnetic anion (*superexchange*). For this effect, we will not consider the outer closed shells of the cations, so that the model is based on a three-center four-electron system.[12]

(c) Indirect exchange between unpaired electrons on the two cations via the closed outer shells of these cations. This effect will be called *indirect valence-shell exchange* and the model is then based on a two-center six-electron system.[13]

In addition, there occur, in principle, cross terms between (b) and (c) involving both the anion and the valence shell of one or two cations. In this paper we will not analyze these cross terms; it is our aim to establish the magnitudes of superexchange and of indirect valence-shell exchange separately and to study their dependence on the geometry of the complex *MXM* and on the extension of the orbitals for the different effective electrons. The components (a)–(c) of the interaction energy are evaluated and added to obtain the magnetic energy for the triplet and singlet states of the complex *MXM*. For the crystal of given symmetry, these interactions are summed over all complexes, for different spin patterns, and then compared to obtain the most stable arrangement.

The interactions are evaluated in first and second orders of exchange-perturbation theory with, for each ion, the ground-state free-ion wave functions as zeroth order (no crystal-field splittings). The zeroth-order wave function for the complex *MXM* is antisymmetric with respect to intra- as well as inter-atomic exchange of electrons; it is an eigenfunction of the symmetrized[8] unperturbed Hamiltonian H_0. The construction of zeroth-order wave functions for the singlet or triplet can be carried out straightforwardly by using projection-operator techniques,[14,15] or directly from properties of a spin-space determinental wave function.[16] We will briefly sketch the projection-operator procedure for the three-center four-electron system.

Let ϕ_a, ϕ_b, and ϕ_c denote the ground-state orbitals for the four effective electrons; ϕ_a and ϕ_c are singly occupied, whereas there are two electrons in ϕ_b. Consider, on the one hand, the $(2^4 = 16)$-dimensional spin space spanned by the four-electron spin functions $\xi(1)\ \xi(2)\ \xi(3)\ \xi(4)$, where ξ can be either α (spin up) or β (spin down). On the other hand, consider the orbital space spanned by the functions $P\chi(1, 2, 3, 4)$, where P runs over the 24 elements of the permutation group $\mathcal{S}_4$ and where $\chi = \phi_b(1) \times \phi_b(2)\,\phi_a(3)\,\phi_c(4)$. The dimension of the space $\{P\chi\}$ is $\frac{1}{2}4! = 12$ (the one-half is due to the fact that the orbital ϕ_b is doubly occupied). The 16-dimensional spin space can be decomposed into subspaces irreducible under the operations of $\mathcal{S}_4$. It is well known that there exists a one-to-one correspondence between these subspaces and the different values of the pair S^2, S_z, where S is the total spin and S_z its z component. Select any one of these subspaces, with orthonormal basis $\{s_i\}$, and let the corresponding irreducible representation of $\mathcal{S}_4$ be Γ. Next, decompose also the orbital space $\{P\chi\}$ into subspaces irreducible under $\mathcal{S}_4$. Select among these subspaces the one (if it exists) whose corresponding irreducible representation is associate to Γ. Denote by $\{\psi_i\}$ an orthonormal basis in that subspace. Then, as is easily shown, the function

$$\Psi = \frac{1}{m^{1/2}} \sum_{i=1}^{m} \psi_i s_i\ , \tag{1}$$

where m is the dimension of Γ, fulfills the conditions that (i) it is completely antisymmetric, and (ii) it is an eigenfunction of S^2 and S_z.

In this manner, the zeroth-order ground-state wave function for the four-electron three-center system (a similar method applies for other systems) can be explicitly constructed. A simplification arises in our case, since the perturbation Hamiltonian is spinless. Then it is sufficient to use, instead of (1) above, the function

$$\Psi^{(0)} = \mathcal{P}\chi\ , \tag{2}$$

where $\mathcal{P}$ is a certain combination of permutation operators for the four electrons of the system. For the triplet state (index T), $\mathcal{P}$ reads

$$\mathcal{P}_T = \tfrac{1}{4}(I - P_{13} - P_{14})(I - P_{34})\ , \tag{3}$$

whereas for the singlet state (index S)

$$\mathcal{P}_S = \tfrac{1}{6}(I - P_{13} - P_{14} + P_{13}P_{24})(I + P_{34})\ . \tag{4}$$

(I is the identity permutation; P_{ij} permutes electrons i and j.) The above expressions for $\mathcal{P}_T$ and $\mathcal{P}_S$ are readily derived from (1), by using the general form of the perturbation expressions for the energy.

The formulas for $\mathcal{P}_T$ and $\mathcal{P}_S$ in the case of two centers and six electrons (one effective electron representing the unpaired electrons of each cation and two spin-paired effective electrons for the closed outer shells) are somewhat more complicated, although their derivation is again straightforward. These expressions read

$$\begin{aligned}\mathcal{P}_T = (I - P_{14}P_{25}P_{36})[I - 2(P_{13} + P_{14} + P_{34}) \\ - P_{36} + P_{13}P_{46} + 2(P_{14}P_{23} + P_{134} + P_{143} \\ + P_{136} + P_{163}) - P_{14}P_{23}P_{56} - P_{1346} \\ - 2P_{1364} - P_{1643}]\ ,\end{aligned} \tag{5}$$

$$\begin{aligned}\mathcal{P}_S = (I + P_{14}P_{25}P_{36})[I - 2(P_{13} + P_{14} + P_{34}) + P_{36} \\ + P_{13}P_{46} + 2P_{14}P_{23} + 4P_{16}P_{23} + P_{14}P_{23}P_{56} \\ + 2(P_{134} + P_{143} - P_{136} - P_{163}) - 4(P_{23}P_{146} \\ + P_{23}P_{164}) + P_{1346} + 2P_{1364} + P_{1643}]\ .\end{aligned} \tag{6}$$

The exchange-perturbation method followed is of the Rayleigh-Schrödinger type,[8] i.e., an expansion of the perturbed wave function and of the energy in terms of integral powers of a smallness parameter λ. The first-order energy, putting $\lambda = 1$, is

$$E_1 = \langle \Psi^{(0)} | H' | \Psi^{(0)} \rangle + C_1\ , \tag{7}$$

and the second-order energy, again for $\lambda = 1$, reads

$$E_2 = -E_{\text{av}}^{-1}[\langle \Psi^{(0)} | H'^2 | \Psi^{(0)} \rangle - \langle \Psi^{(0)} | H' | \Psi^{(0)} \rangle^2] + C_2\ , \tag{8}$$

where E_{av} is an Unsöld average energy, defined by the procedure of averaging over all excited states for the complex MXM. C_1 and C_2 are correction terms containing H' to higher order than occurring in the leading term of E_1 and E_2, respectively; these terms will be neglected.[8] The perturbation H' is symmetric under permutations of the electrons between the three ions M, X, M. The ground-state wave function $\Psi^{(0)}$ is given by (2), with $\mathcal{P}$ the appropriate projection operator. For the moment, the Unsöld energy will be left as a parameter in the second-order expressions.

The neglect of crystal-field effects leads us to using spherically symmetric functions for the unperturbed atomic orbitals ϕ. For simplicity we adopt a Gaussian form,

$$\phi(r) = (\beta/\pi^{1/2})^{3/2}\, e^{-\beta^2 r^2/2}\ , \tag{9}$$

where r is the distance from the effective electron to its nucleus and β is a characteristic parameter.[17] In the case of a three-center four-electron system we must use two Gaussian parameters: β for the diamagnetic anion and β' for the orbital of the effective d or f electron on the paramagnetic cation. It appears that an essential parameter in the model is the ratio $\gamma = (\beta'/\beta)^2$, which is a measure of the "magnetic size" of the cation with respect to the size of the anion. If $\gamma > 1$, the diamagnetic anion is "larger" than the cation, whereas for $\gamma < 1$ the situation is reversed. For the moment, β and β' are parameters of the model, i.e., no projection is as yet made on real systems. For the case of a two-center six-electron system the Gaussian parameter for each magnetic electron is again β'; the parameter for the closed outer shells of each cation is denoted by β_c. Then $\gamma' = (\beta'/\beta_c)^2$ is a measure of the magnetic size of the cation with respect to the extension of its outer closed shells. Since the orbitals of $4f$ electrons are embedded inside the valence shells we expect $\gamma' > 1$ for such systems. On the other hand, for $3d$ electrons $\gamma' < 1$.

III. INDIRECT EXCHANGE VIA THE ANION (SUPEREXCHANGE)

We consider first the exchange interaction between two $3d$ or $4f$ electrons in the presence of a diamagnetic anion, on the basis of a three-center four-electron system. Each triplet (abc) of two cations and one anion is characterized by its geometric configuration; it may form an isosceles triangle (with respect to the site of the anion) or a nonisosceles triangle. Let R denote the smaller of the cation-anion distances and Y (>1) their ratio. This yields, in total, the dimensionless parameters γ, βR, Y, and θ. For each triplet of ions in the solid we carry out the calculations of the interaction energy in first and second orders of perturbation theory. The first-order integrals are easy to compute; those of second order are determined following methods developed by Zimering.[18]

Let us denote the interaction energy for a given triplet (abc) in first order by $E_1\,(abc)$ and in second order by $E_2\,(abc)$. In either order, these energies are evaluated both for the triplet (T) and singlet (S) configurations of the spins on the two magnetic cations. The perturbation energies are then denoted by E_{1T}, E_{2T}, E_{1S}, and E_{2S}, respectively.

The quantity of interest is the "effective" interaction between the magnetic ions a and c, i.e., their interaction as modified by the presence of the diamagnetic anion b. Let $\mathcal{E}_1(ac)$, $\mathcal{E}_2(ac)$ denote this effective interaction in first and second orders, respectively, with an additional subscript T or S for the two possible spin configurations. Then we have, by definition,

$$\mathcal{E}_1(ac) = E_1(abc) - [E_1^{(0)}(ab) + E_1^{(0)}(bc)]\,, \tag{10}$$

where $E_1^{(0)}(ab)$ is the first-order pair interaction between a and b; and $E_1^{(0)}(bc)$ that between b and c, i.e., without the presence of the third particle. No subscripts T or S are needed for the pair interactions $E_1^{(0)}(ab)$ and $E_1^{(0)}(bc)$, as these do not depend on the spin of the paramagnetic cations.

We can therefore write

$$\begin{aligned}\mathcal{E}_{1T}(ac) &= E_{1T}(abc) - [E_1^{(0)}(ab) + E_1^{(0)}(bc)]\,,\\ \mathcal{E}_{2T}(ac) &= E_{2T}(abc) - [E_2^{(0)}(ab) + E_2^{(0)}(bc)]\end{aligned} \tag{11}$$

and

$$\begin{aligned}\mathcal{E}_{1S}(ac) &= E_{1S}(abc) - [E_1^{(0)}(ab) + E_1^{(0)}(bc)]\,,\\ \mathcal{E}_{2S}(ac) &= E_{2S}(abc) - [E_2^{(0)}(ab) + E_2^{(0)}(bc)]\,.\end{aligned} \tag{12}$$

From (11) and (12) it is seen that the "effective" interactions also contain the direct exchange between the two paramagnetic cations. In the following the name "superexchange" will, for simplicity, also include this direct interaction. The second-order energies involve a summation over excited states or, alternatively, they are expressed in terms of Unsöld energies (for direct and indirect exchange, respectively, depending also on the spin configurations), which quantities cannot be directly calculated on the basis of the model. These average energies are taken as equal in the triplet and singlet configurations; this assumption is consistent with the interpretation of the average energy as a promotional or excitation energy of an electron.

We first present numerical results for an isolated triplet of ions forming an isosceles triangle. In Fig. 1 we compare, for a triplet (abc), the effective interactions between the cations a and c $[\mathcal{E}(ac)]$ with their interaction $[E^{(0)}(ac)]$ in the absence of the diamagnetic anion, as a function of $\cos\,\theta$, with θ the opening of the isosceles triangle at the anion. Results, in units of $e^2\beta$, are given both for triplet (T) and singlet (S) spin ordering of the cations in first order of perturbation. In Figs. 1(a) and 1(b), $\beta R = 2$ and $\gamma = 0.5$ (diamagnetic anion "smaller" than the magnetic size of the cation), whereas in Figs. 1(c) and 1(d), $\beta R = 2$ and $\gamma = 2$ (diamagnetic anion "larger").

We see from Figs. 1(a) and 1(b) that for $\gamma = 0.5$ the effective interaction in case of parallel spins is less repulsive than the pair interaction (anion absent). The effective interaction becomes even attractive for opening $\theta \gtrsim 80°$. This illustrates the effect of superexchange as given by the model. For antiparallel spins the first-order pair interaction shows again the typical Heitler-London dependence on the distance between the cations. In this case, the attraction is strongly reduced by the presence of the anion, except for large values of the opening. From Figs. 1(c) and 1(d) we see that the pair interaction is negligible for $\theta \gtrsim 80°$. For triangles of large opening, the interaction is then completely determined by the presence of the anion; it is repulsive for the triplet and attractive for the singlet case. If $\theta \lesssim 80°$, the effective interaction for parallel spins is less repulsive than the pair interactions, even becoming attractive; in the antiparallel case the effective interaction is less attrac-

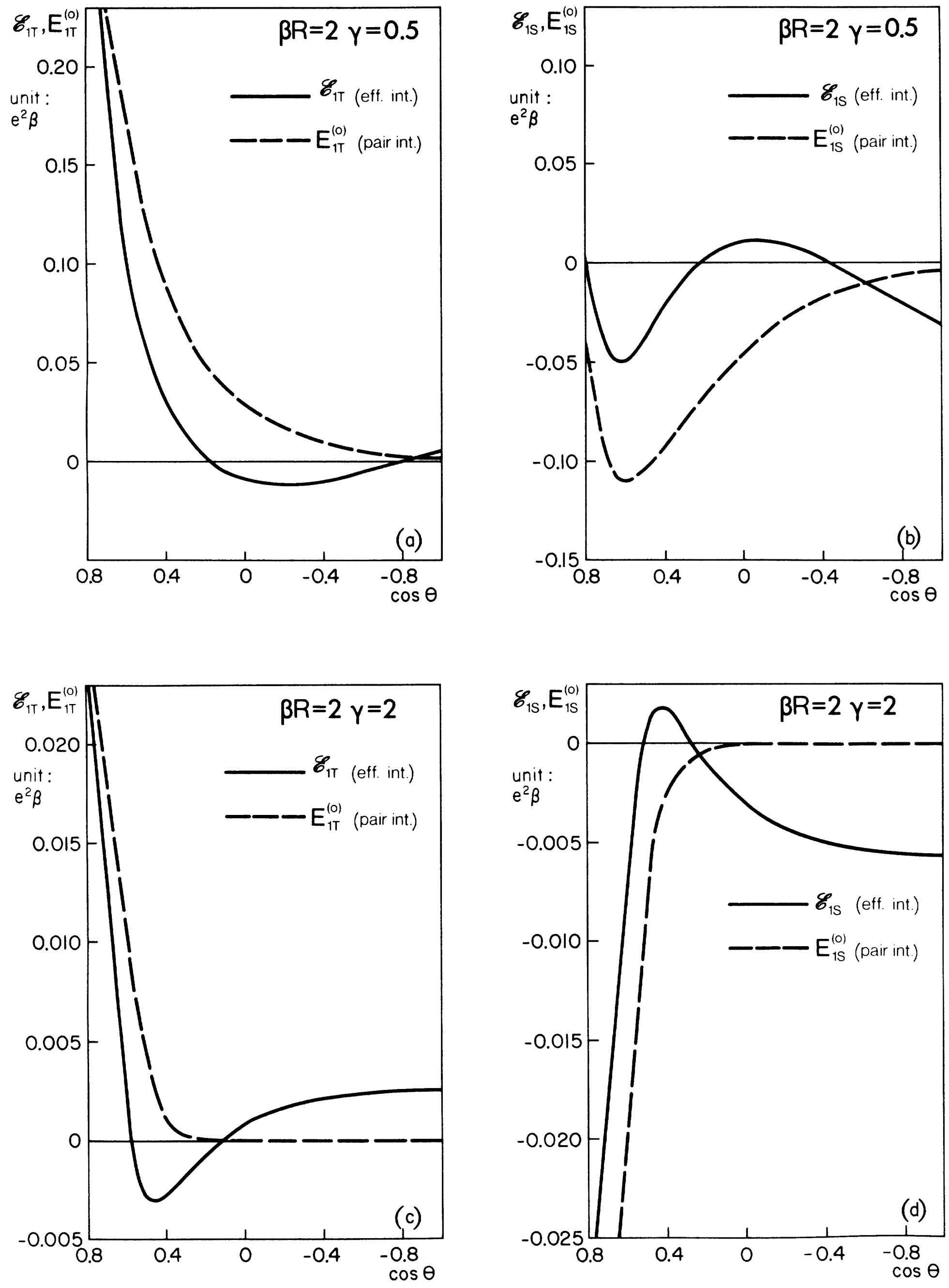

FIG. 1. Effective first-order interactions between two paramagnetic cations with parallel spin alignments, $\mathcal{E}_{1T}$, and antiparallel spin alignment, $\mathcal{E}_{1S}$, as compared with the respective cation pair interactions $E_{1T}^{(0)}$ and $E_{1S}^{(0)}$, as a function of $\cos\theta$, where θ is the opening of the isosceles triangle at the diamagnetic anion. The Gaussian parameters are $\beta R = 2$, $\gamma = 0.5$ [Figs. 1(a) and 1(b)] and $\beta R = 2$, $\gamma = 2$ [Figs. 1(c) and 1(d)].

tive than the pair interaction, even becoming repulsive.

We conclude from Fig. 1 that the first-order interaction between two Gaussian atoms with one effective electron each (spins parallel or antiparallel) is significantly modified, because of superexchange, by the presence of a diamagnetic anion with two effective electrons. The contribution by indirect exchange alone can be obtained from the figures by subtracting the two curves. Similar results were obtained for other values of γ in the interval 0.4 to 10 and βR between 1 and 5; these intervals for γ and βR cover the applications to be discussed later.

Next we compare, in Figs. 2 and 3, the effective

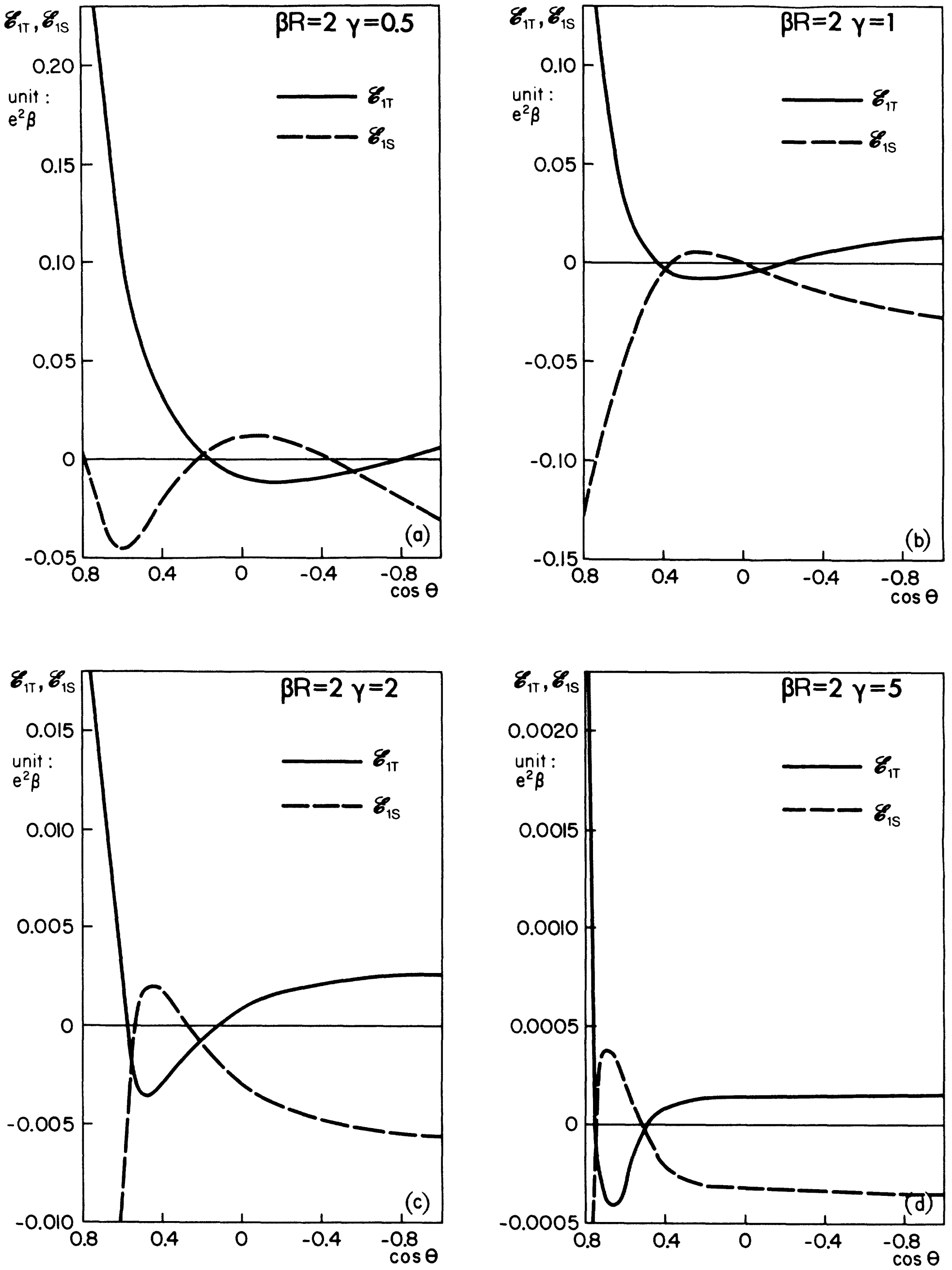

FIG. 2. Comparison between effective first-order cation interactions for parallel ($\mathcal{E}_{1T}$) and antiparallel ($\mathcal{E}_{1S}$) spin alignments, as a function of cosθ, for an isolated triplet. The Gaussian parameters are $\beta R = 2$, $\gamma = 0.5$ [Fig. 2(a)], $\gamma = 1$ [Fig. 2(b)], $\gamma = 2$ [Fig. 2(c)], and $\gamma = 5$ [Fig. 2(d)].

cation-cation interaction in first and second orders for parallel and antiparallel spins and for an isolated triplet, as a function of cosθ. The βR value is kept constant at 2 and the values of γ are 0.5, 1, 2, and 5, respectively.

The first-order results (Fig. 2) show that either the parallel or the antiparallel coupling has the lower energy, depending sensitively on the opening θ of the triangle and on the value of γ. We note that the 180° superexchange gives in most cases the dominant contribution to the magnetic energy, even on the basis of spherically symmetric orbitals for the effective electrons.

Upon increasing γ, the interval of values of the opening θ for which the parallel alignment is more stable, becomes smaller, while shifting to smaller

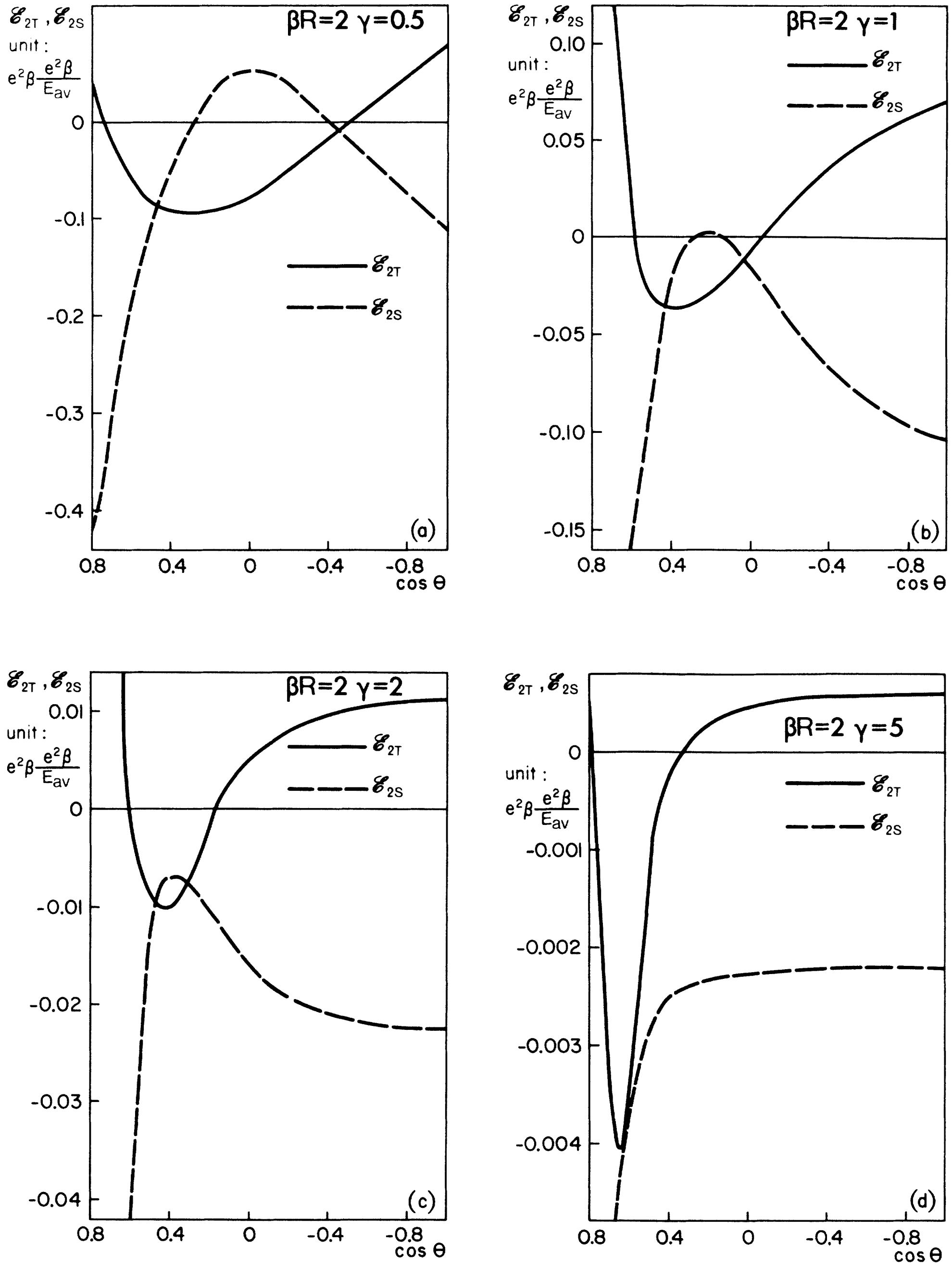

FIG. 3. Same comparison as in Fig. 2, but this time for second-order effective interactions ($\mathcal{E}_{2T}$ and $\mathcal{E}_{2S}$, respectively). The parameters have the same values as in Fig. 2.

angles. Therefore, when considering a crystal and summing over all the possible triplets, it is predicted that, on the basis of superexchange alone, the ferromagnetic spin alignment can be the more stable one *only for low values of* γ (i.e., relatively "large" paramagnetic cations). It will be found that this condition is not fulfilled for salts with 3*d* or 4*f* cations, i.e., that superexchange alone will always give rise to antiferromagnetic alignment of the unpaired spins. No general conclusion can be drawn regarding relative stability of possible different antiferromagnetic spin structures, since they are characterized by different combinations of triangles (*abc*) with parallel and antiparallel spins on the cations.

It is interesting to observe, by comparing Figs. 2 and 3, that the second-order results are similar to those in first order. In view of this similarity, we expect that, in a first approach, and on the basis of superexchange interactions alone, stability criteria for different types of magnetic ordering can be established on the basis of *first-order* interactions only. This eliminates the necessity of considering the second-order contributions, containing the unknown quantity[19] $e^2\beta/E_{av}$, separately. The results obtained for other βR values in the range 1–5 are very similar to those given in Figs. 2 and 3.

We have also calculated, in first and second orders, the effective interaction for nonisosceles triangles; this was done for the same range of βR and γ values as for isosceles triangles. The ratio Y was varied in the range 1.1–2. The results are again similar in both orders of perturbation, and exhibit the same characteristics as for isosceles triangles.

The results obtained in this section show that the superexchange energy for a complex MXM varies strongly with respect to varying the opening angle θ of the triangle. Thus, it is not *necessary* to start from oriented crystal-field orbitals for the electrons to explain such a variation.

IV. INDIRECT EXCHANGE VIA CATION VALENCE SHELLS

Next we consider the exchange interactions between two $3d$ or $4f$ unpaired electrons on two different cations via the closed outer shells of the same cations, on the basis of a two-center six-electron system. The zeroth-order wave function is again of the form (2), with $\mathcal{P}$ given by (5) or (6). The parameters are here $\beta' R'$, with β' the Gaussian parameter for the magnetic electron and R' the cation-cation distance, and $\gamma' = (\beta'/\beta_c)^2$, with β_c the Gaussian parameter for the closed cation shells.

Again, only an effective indirect exchange is considered, by subtracting all nonmagnetic terms (i.e., those terms which are the same between the singlet and triplet configurations) from the first- and second-order perturbation energies. The results are given in Figs. 4 and 5 with a fixed value $\beta' R' = 4.5$ and $\beta' R' = 8$, respectively, and varying γ' between 0 and 20. The value of $\gamma' = 1$ is, of course, excluded by the Pauli principle, but it is found that the perturbation energies vary continuously near that point. The first-order results, denoted by $\mathcal{E}'_{1T}$ and $\mathcal{E}'_{1S}$, respectively, are given in units of $e^2\beta'$, whereas $e^2\beta'(e^2\beta'/E'_{av})$ is the unit of second-order energy, with E'_{av} again an Unsöld energy. The direct exchange between the unpaired electrons is not given in the figures, as it is several orders of magnitude smaller than the indirect exchange interaction.

We observe again a striking similarity between the results in first and second orders. In addition, a singlet-triplet inversion occurs for a range of values for γ' depending on the chosen value for $\beta' R'$. Keeping the size of the magnetic orbital, as well as the cation-cation distance, fixed (constant $\beta' R'$) and increasing γ' means that the closed cation shells expand. The limit for $\gamma' \to 0$ corresponds to the system of two magnetic electrons only in the field of two nuclei of charge +1. The $\gamma' \to \infty$ corresponds to the system of two magnetic electrons in the field of two nuclei of charge +3. As a distinction between $3d$ and $4f$ electrons we can roughly take $\gamma' \approx 1$; the d-electrons have γ' values smaller and the f-electron γ' values larger than this limiting value.

In the specific case of EuO we estimate (see below) γ' to be of the order of 2.5 and $\beta' R' \approx 6.0$, whereas for MnO, γ' is approximately 0.5 and $\beta' R' \approx 4.5$. From Figs. 4 and 5 we then see that for EuO (and, generally, for $4f$ electrons) and nearest-neighbor cations the triplet state is definitely the more stable one. For further neighbors, the singlet-triplet inversion occurs at higher values of γ' and the energies decrease very rapidly. This explains why the ferromagnetic coupling between Eu^{2+} ions becomes less important upon substituting a larger anion. The model thus gives an interpretation of the ferromagnetic cation-cation coupling discussed in Sec. I. In the case of MnO (and, generally, for $3d$ electrons) we note from Fig. 4 that the effect of indirect valence-shell exchange is much smaller; for these compounds the magnetic pattern is then mainly determined by the superexchange interaction. The effect of the indirect valence-shell exchange reflects itself here in a lowering of the transition temperature for the antiferromagnetic structure.

On the basis of the results of this section and Sec. III, it is concluded that the magnetic interactions in solids with $3d$ and $4f$ cations can in principle be explained on the basis of the same model. For these compounds the resulting magnetic order depends upon a balance between a ferromagnetic indirect exchange via the valence shells of the cations and an antiferromagnetic indirect exchange via the anion.

V. MAGNETIC ORDERING AND TRANSITION TEMPERATURES

The results given in Secs. III and IV regarding exchange interactions between unpaired $3d$ or $4f$ electrons on two different cations via a diamagnetic anion (superexchange) and via the closed outer shells of the cations (indirect valence-shell exchange) will now be applied to the determination of the most stable spin arrangement in the solids of composition MX of such compounds.[20] The dominant crystal structure, both with $3d$ and $4f$ compounds, is $B1$ (NaCl); of those which crystallize in structures different from $B1$, we mention MnS

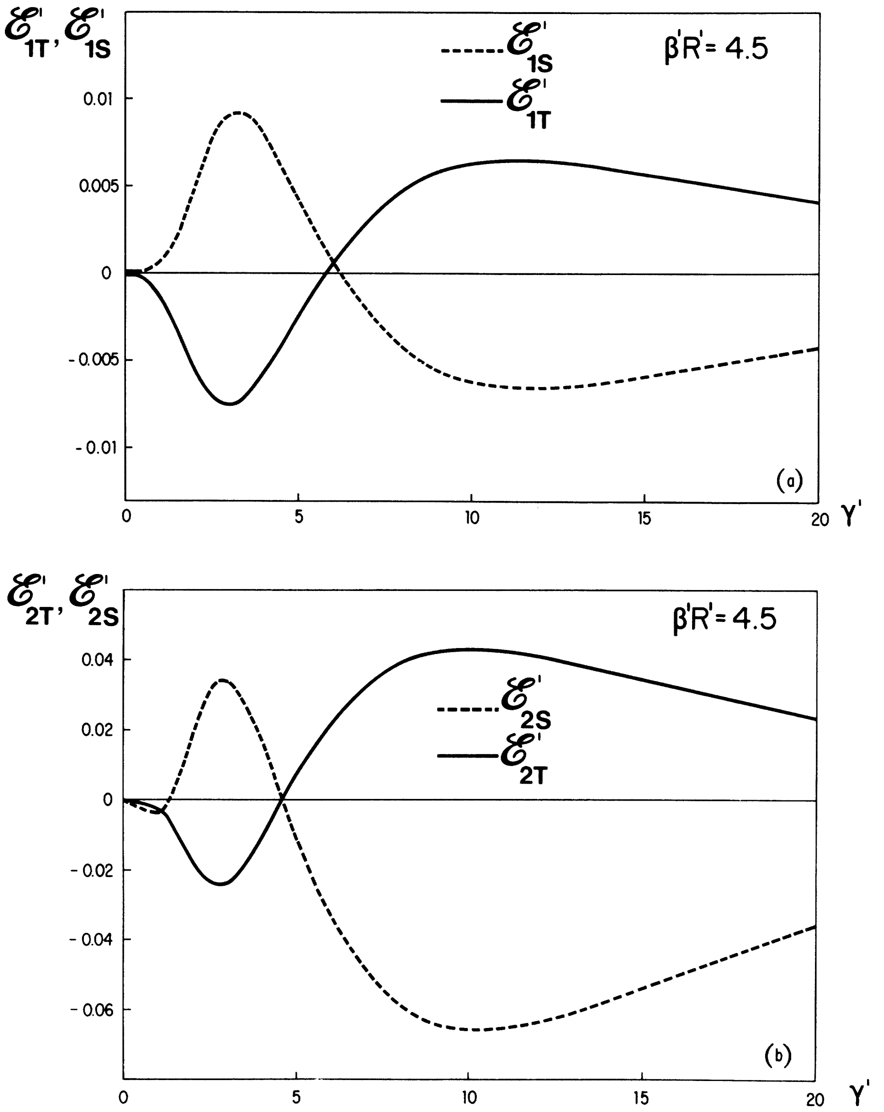

FIG. 4. Effective indirect exchange via cation valence shells in first order [Fig. 4(a)] and second order [Fig. 4(b)] of perturbation theory for singlet $(\mathcal{E}'_S)$ and triplet $(\mathcal{E}'_T)$ configurations of the spins as a function of $\gamma' = (\beta'/\beta_c)^2$, where β' is the Gaussian parameter of the magnetic electron and β_c of the closed cation shells; $\beta'R' = 4.5$, with R' the cation-cation distance. (Direct exchange is too small to be shown on this scale.) In (a), the energy unit is $e^2\beta'$, and in (b) the unit is $e^2\beta'(e^2\beta'/E'_{\mathrm{Av}})$.

and MnSe which possess, in addition to a $B1$-modification, the $B3$ (sphalerite) and $B4$ (wurtzite) structures. Further, a number of compounds are found with the $B8$ (NiAs) structure. The large majority of the compounds with the $B1$ structure exhibits at the lowest temperatures antiferromagnetic ordering of the second kind, in which one-half of the first neighbors have spins parallel to that of the reference cation, the other half antiparallel. All second neighbors are antiparallel to the spin of the reference cation. This is one of four possible antiferromagnetic structures in the $B1$ lattice.[21] For the $3d$ compounds the only known exception is CrN, which is antiferromagnetic of the fourth kind. All $4f$ compounds which are nonconductors crystallize in the $B1$ structure and most of them also exhibit antiferromagnetic ordering of the second kind. A few (EuO, EuS, and GdN) are ferromagnetic, as mentioned earlier, whereas EuSe and some others show a more complicated behavior. The Néel temperatures are of the order of a few hundred degrees Kelvin for the $3d$ compounds and between a few and 30° for the rare-earth compounds. All nonconducting compounds with structures different from $B1$ are antiferromagnetic and have transition temperatures similar to those with the $B1$ structure.

It is convenient to analyze stability of the different possible spin patterns in terms of transition temperatures from the ordered to the disordered structures (Néel or Curie temperatures), the pattern with the highest transition temperature being the most stable one. To evaluate transition temperatures we adopt a molecular-field approximation and write the magnetic part of the molar crystal energy in the form

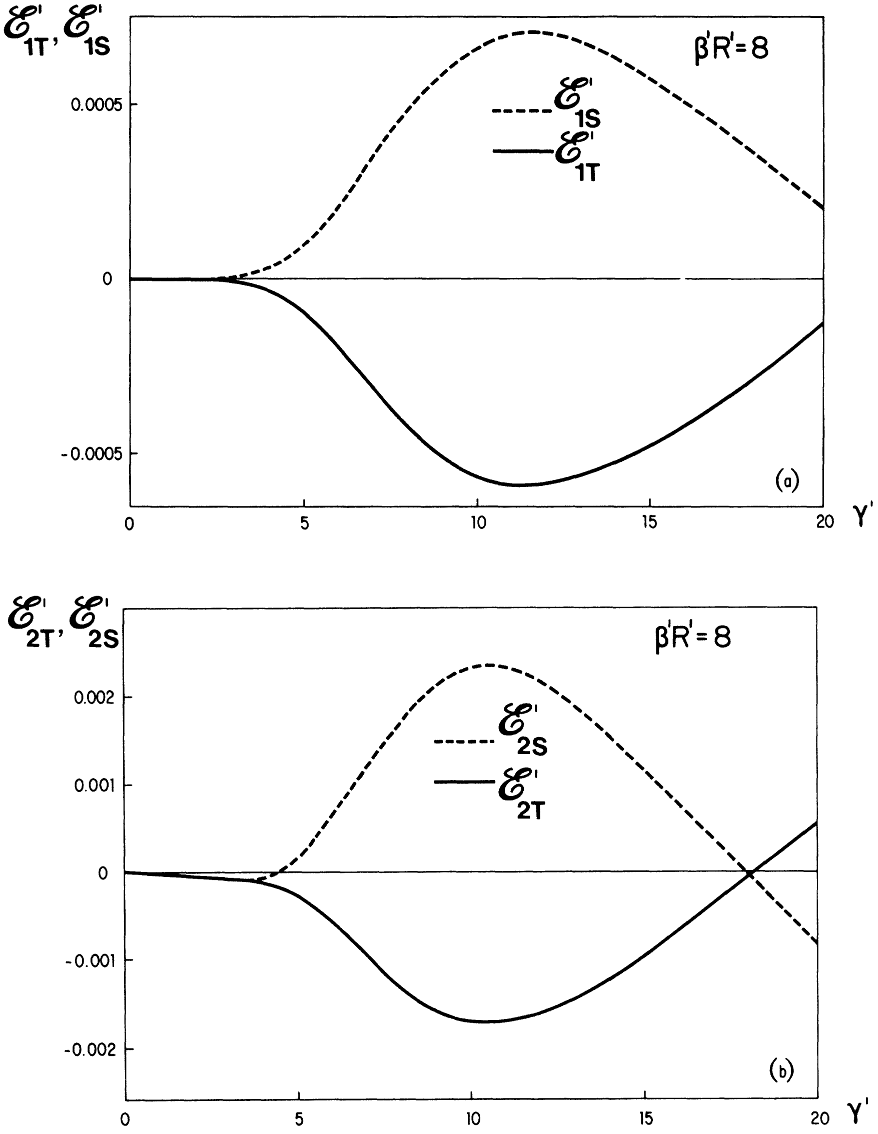

FIG. 5. Same effects as in Fig. 4, but for $\beta' R' = 8$. (Direct exchange is too small to be shown on this scale.) Units are the same as in Figs. 4(a) and 4(b), respectively.

$$-N\sum_{c\neq a} \mathcal{J}_{ac}\vec{S}_a \cdot \vec{S}_c \ , \tag{13}$$

(N is Avogadro's number), where a denotes a reference cation, c any other cation of the crystal, and $\vec{S}_a$, $\vec{S}_c$ their spin operators. In this notation, $\mathcal{J}_{ac}$ is one-half the energy difference between the singlet and triplet configurations per pair of magnetic electrons between a and c; this quantity can be obtained from the coupling parameters of the effective-electron model by dividing through n^2, where n is the number of unpaired electrons per cation. The quantity $\mathcal{J}_{ac}$ can be written in the form

$$\mathcal{J}_{ac} = J^{(0)}_{ac} + \sum_b \mathcal{J}_{b(ac)} + \mathcal{J}'_{ac} \ , \tag{14}$$

where $J^{(0)}_{ac}$ is the contribution due to direct exchange between the spins on a and c, $\mathcal{J}_{b(ac)}$ the indirect-exchange contribution through the anion b, and where $\mathcal{J}'_{ac}$ results from indirect exchange via the closed outer shells of the cations a and c. Using the notation for the energies of the complex MXM employed in Secs. I–IV, and limiting ourselves to first-order perturbation effects, we have

$$J^{(0)}_{ac} = (1/2n^2)(E^{(0)}_{1S} - E^{(0)}_{1T}),$$

$$\mathcal{J}_{b(ac)} = (1/2n^2)(\mathcal{E}_{1S} - \mathcal{E}_{1T}) - J^{(0)}_{ac},$$

$$\mathcal{J}'_{ac} = (1/2n^2)(\mathcal{E}'_{1S} - \mathcal{E}'_{1T}) - J^{(0)}_{ac} \ . \tag{15}$$

These quantities can, therefore, be directly calculated from the model.

As an example consider the structure $B1$. To carry out the crystal summation one must first de-

TABLE I. Different possible spin arrangements expressed by the number of cations, for each shell, with parallel and antiparallel spins with respect to a reference cation, for the structure *B*1.

	number of cations with spin parallel and antiparallel to that of the reference cation							
	First neighbors		Second neighbors		Third neighbors		Fourth neighbors	
Kind of magnetic order	↑↑	↑↓	↑↑	↑↓	↑↑	↑↓	↑↑	↑↓
ferromagnetic	12	0	6	0	24	0	12	0
antiferromagnetic								
first kind	4	8	6	0	8	16	12	0
second kind	6	6	0	6	12	12	12	0
third kind	4	8	4	2	16	8	4	8
fourth kind	6	6	2	4	12	12	4	8

termine, for each of the four possible antiferromagnetic spin patterns, the numbers of cations around a reference cation, in consecutive shells, with spin parallel or antiparallel to that of the reference cation. These numbers are given, up to and including fourth neighbors, in Table I.

Let $T_{N,1}$, $T_{N,2}$, $T_{N,3}$, and $T_{N,4}$ denote the Néel temperatures for the four antiferromagnetic structures, and T_C the Curie temperature. It is convenient to relabel $\mathcal{J}_{ac}$ as $\mathcal{J}_1$ if *c* is a nearest neighbor of the reference cation *a*, as $\mathcal{J}_2$ if *c* is a second neighbor, etc. The transition temperatures, in the molecular-field approximation, can then readily be obtained from Table I, extending formulas given by Smart.[22] These expressions read

$$\begin{aligned}
\rho_S T_C &= 12\mathcal{J}_1 + 6\mathcal{J}_2 + 24\mathcal{J}_3 + 12\mathcal{J}_4 \,, \\
\rho_S T_{N,1} &= -4\mathcal{J}_1 + 6\mathcal{J}_2 - 8\mathcal{J}_3 + 12\mathcal{J}_4 \,, \\
\rho_S T_{N,2} &= -6\mathcal{J}_2 + 12\mathcal{J}_4 \,, \qquad (16) \\
\rho_S T_{N,3} &= -4\mathcal{J}_1 + 2\mathcal{J}_2 + 8\mathcal{J}_3 - 4\mathcal{J}_4 \,, \\
\rho_S T_{N,4} &= -2\mathcal{J}_2 - 4\mathcal{J}_4 \,,
\end{aligned}$$

with $\rho_S = 3k/2S(S+1)$ and *k* the Boltzmann constant. For the analysis of magnetic stability at 0 °K we can, of course, also use the exchange interactions as given by the model directly, i.e., without adopting a molecular-field approximation.

All anions of the lattice contribute in principle to every $\mathcal{J}_i$ through superexchange, but it is found that the summation over the anions may be limited to a very few terms. First, it is found that in summing over the anions the contribution to $\mathcal{J}_i$ arising from triplets *MXM* which form nonisosceles triangles with respect to the site of the anion, is negligible. In addition, superexchange contributions to $\mathcal{J}_i$ with $i > 2$ are negligibly small in all cases considered. There are only two anions which contribute significantly to $\mathcal{J}_1$, with *MXM* opening angle $\theta = 90°$ at the anion (90° superexchange), whereas only one anion must be considered for $\mathcal{J}_2$, with opening angle $\theta = 180°$ (180° superexchange). The indirect valence-shell exchange is mostly negligible except if the two cations are nearest neighbors.

To obtain numerical results the values of the Gaussian parameters β (anion size), β' (paramagnetic size of the cation), and β_c (diamagnetic cation size) must be determined. We will use the following semiempirical approach. In previous work on the crystal stability of ionic solids of II-VI compounds,[23] the β values for the ions O^{2-}, S^{2-}, Se^{2-}, Te^{2-} were estimated from the values of the diamagnetic susceptibilities χ relative to those of the rare-gas atoms. For O^{2-}, with two effective electrons, this yields an estimated β value somewhat less than 1 Å^{-1}; those of the other ions are correspondingly smaller. Let us adopt a gauge value $\beta = 1$ Å^{-1} for O^{2-}; the β values for the other ions can, in principle, be estimated on the basis of their diamagnetic susceptibilities (proportional to β^{-2} in the model) relative to the value for O^{2-}, by using the relation $\beta_{S^{2-}} = \beta_{O^{2-}}(\chi_{O^{2-}}/\chi_{S^{2-}})^{1/2}$, and similarly for the other anions. In view of the fact, however, that values of χ for these ions are not known with any precision, this procedure leads at best to a range of possible β values. On the other hand, to estimate the Gaussian parameters β' of the magnetic electron and β_c of the cation core we have evaluated the contributions of the different electron shells to the diamagnetic susceptibilities, using Hartree-Fock self-consistent field (SCF) functions as given by Herman and Skillman.[24] For comparison with experiment of the results obtained with the present model, we choose again the Mn^{2+} and Eu^{2+} ions as examples. The above procedure leads to a value of γ', which for Mn^{2+} is found to be 0.5 and for Eu^{2+} to be 2.5. The β' and β_c values can then again be calculated with respect to the gauge value of $\beta = 1$ Å^{-1} for O^{2-} in the manner described above. The results for the solids of the Mn and Eu chalcogenides based on these values of the Gaussian parameters show that the observed stable spin structures are reproduced by the model, except for EuS which is predicted to be antiferro-

TABLE II. Results for coupling coefficients $\mathcal{J}_1$ and $\mathcal{J}_2$, stable magnetic structure and transition temperatures obtained on the basis of the present model as compared with experiment. Values of the nearest-neighbor distance R_0 (anion–cation) and of the Gaussian parameters β (anion), β' (magnetic electron), and β_c (cation core) are also given. Stable magnetic structures are ferromagnetic (F) and antiferromagnetic of the second type (AF2).

Compound	Nearest-neighbor distance R_0 (Å)	Gaussian parameters (Å^{-1}) Cation β'		Anion β	Coupling coefficients (°K) $\mathcal{J}_1$ Calc.	$\mathcal{J}_1$ Expt.	$\mathcal{J}_2$ Calc.	$\mathcal{J}_2$ Expt.	Stable magnetic structure Calc.	Stable magnetic structure Expt.	Transition Temperature (°K) Calc.	Transition Temperature (°K) Expt.
		β'	β_c	β								
MnO	2.22	1.40	1.95	1.08	−1.1	−5.65[a]	−3.8	−5.65[a]	AF2	AF2[b]	135	122[b]
MnS	2.61	1.40	1.95	0.77	−7.0		−4.2		AF2	AF2[b]	144	154[b]
MnSe	2.72	1.40	1.95	0.68	−9.4		−5.2		AF2	AF2[b]	181	173[b]
EuO	2.57	1.62	1.03	1.08	2.6	$\left\{\begin{matrix}0.65^{c}\\0.75\end{matrix}\right\}$	−0.03	−0.06[c]	F	F[c]	332.8	69.4[c]
EuS	2.98	1.62	1.03	0.77	0.12	0.20[c]	−0.09	$\left\{\begin{matrix}-0.08^{c}\\-0.10\end{matrix}\right\}$	F	F[c]	9.9	16.5[c]
EuSe	3.10	1.62	1.03	0.68	−0.19	0.13[c]	−0.18	−0.11[c]	AF2	F, AF2[c]	11.3	2.8, 4.6[d]
EuTe	3.30	1.62	1.03	0.60	−0.35	0.03[c]	−0.20	−0.17[c]	AF2	AF2[c]	12.5	8.0–11.0[c]

[a] See Ref. 26.

[b] Landolt-Boernstein, *Numerical Data and Functional Relationships* (Springer-Verlag, Berlin, 1966), new series G. II, Vol. 2.

[c] See Ref. 2.

[d] EuSe is ferromagnetic below 2.8 °K and antiferromagnetic (of the second kind) between 2.8 and 4.6 °K.

magnetic of the second kind (AF2). EuO is definitely ferromagnetic on this basis. The calculated transition temperatures are, however, all too high by an order of magnitude, suggesting that the chosen values for the Gaussian parameters are all somewhat too low. Upon increasing these values it appears that the results for the transition temperatures, and sometimes also those for relative stability of the different possible spin structures, change very rapidly. In Table II we present the results for those modified Gaussian parameters which give considerable agreement with experiment. Also listed in the table are results for the coupling parameters $\mathcal{J}_1$ and $\mathcal{J}_2$ separately. Further small adjustments of the β parameters would very probably lead to still better agreement with experiment, but the physical significance of such a procedure is very doubtful, also in view of the fact that we are limiting ourselves to a first-order calculation. On the other hand, the experimental observations (a) that EuS (and EuO) are ferromagnetic, (b) that[25,26] $\mathcal{J}_1 < 0$ for Mn^{2+}, $\mathcal{J}_1 > 0$ for V^{2+} in MgO, and (c) that the Néel temperatures increase in the series MnO, MnS, MnSe, severely limit the possible ranges of values for the Gaussian parameters in the model, if the parameter γ' is kept constant. In particular, it turns out that under those limitations ferromagnetic behavior of EuS implies an overestimate of $\mathcal{J}_1$ and thus of the Curie temperature T_C, for EuO.

The transition temperatures listed in Table II were calculated with the values $S=\frac{5}{2}$ for Mn^{2+} and $S=\frac{7}{2}$ for Eu^{2+}. We note from the table that the signs of the coupling parameters $\mathcal{J}_1$ (90° configuration of two cations with respect to a central anion) and $\mathcal{J}_2$ (180° configuration of the cations), as calculated on the basis of the model, agree with experiment. In addition, the magnitudes of these parameters are in relatively good agreement, although, e.g., for EuO the ferromagnetic indirect valence-shell exchange is somewhat overestimated. The predicted stable magnetic structures are the same as those observed, with the exception that the transition from ferromagnetic to antiferromagnetic stability of the Eu salts is predicted to occur between the sulfide and the selenide, whereas experimentally EuSe is still ferromagnetic up to 2.8 °K and antiferromagnetic (of the second kind) between 2.8 and 4.5 °K.

For the Mn series it is observed from Table II that the model reproduces the observed increase in Néel temperature with increasing size of the anion. This can be understood on the basis of the two components of the exchange energy: Whereas the anion-independent indirect valence-shell exchange decreases rapidly with increasing cation-cation distance, the antiferromagnetic superexchange becomes more important upon substituting a heavier anion. This more than compensates the decrease in superexchange with increase in anion-cation distance.

It has recently been observed[25] from accurate NMR measurements on V^{2+} in MgO that $\mathcal{J}_1$, although small, is of positive sign. This fact provides a further sensitive test case regarding the validity of the present model. By following exactly the same procedure as for the Mn^{2+} and Eu^{2+} cations, we find for V^{2+} from SCF wave functions a γ' value of 0.75 and estimate β' to be between 1.4 and 1.45 Å^{-1}, with the corresponding values for β_c of 1.62 and 1.67 Å^{-1},

TABLE III. Results for coupling coefficients $\mathcal{J}_1$ and $\mathcal{J}_2$ obtained on the basis of the present model as compared with experiment. The contributions to $\mathcal{J}_1$ and $\mathcal{J}_2$ arising from direct exchange, superexchange, and indirect valence-shell exchange are listed separately. Values of Gaussian parameters are also given. Host crystal is MgO, with $R_0 = 2.10$ Å. The two values for β' and the corresponding values for β_c bracket an estimated range for V^{2+}.

				$\mathcal{J}_1$ (°K)					$\mathcal{J}_2$ (°K)				
				Calculated					Calculated				
Impurity	Gaussian parameters (Å^{-1}) β'	β_c	β	Direct exch.	Super-exch.	Indirect valence shell exch.	Total	Expt.	Direct exch.	Super-exch.	Indirect valence shell exch.	Total	Expt.
Mn^{2+}	1.40	1.95	1.08	0.1	−7.6	4.5	−3.0	−14[a]	0	−9.2	0	−9.2	−14[a]
V^{2+}	1.40	1.62	1.08	0.4	−21.4	32.2	11.2	5.3[b]	0	−25.7	1.0	−24.7	−36.1[b]
V^{2+}	1.45	1.67	1.08	0.3	−19.8	34.7	15.2	5.3[b]	0	−20.1	1.3	−18.8	−36.1[b]

[a] Reference 16.

[b] Reference 25.

respectively. For comparison, we also consider Mn^{2+} in a MgO lattice, for which the values of $\mathcal{J}_1$ and $\mathcal{J}_2$ have also been measured.[26] The results of the calculations are given in Table III, with the different exchange contributions to these coupling parameters listed separately.

Again, the signs of $\mathcal{J}_1$ and $\mathcal{J}_2$, as well as their order of magnitude, are predicted correctly by the model. We also note that for $\mathcal{J}_2$ (180° configuration) the direct and indirect valence-shell exchanges are negligible, which is to be expected. The sign of $\mathcal{J}_2$ is then determined entirely by superexchange effects.

As already mentioned, a configuration-interaction calculation of V^{2+} in MgO has been carried out by Huang Liu and Orbach[7] who found a net value for $\mathcal{J}_1$ of 9 °K. This value results from several components of the singlet-triplet energy difference of either sign. A large ferromagnetic contribution ($\mathcal{J} = +256$ °K) arises from the ionic configuration (no transfer) due to interactions involving p_x (and, in turn, p_z) orbitals on a ligand anion and d_{xz} orbitals on two cations in a 90° configuration. In addition, they establish a considerable antiferromagnetic cation-cation direct exchange ($\mathcal{J} = -164$ °K), due to the nonorthogonality of the cation wave functions (Heitler-London). These two terms correspond in our perturbation treatment to the sum of first-order effects. Taking into account also anion-cation and cation-cation transfer contributions, such terms are found to be considerably smaller and to favor the antiparallel spin arrangement of the cations. For one of the possible types of anion-cation transfer these authors establish a reversal of the sign as predicted by the Goodenough-Kanamori rules, again because of nonorthogonality of the cation wave function. Such transfer terms are implicitly contained in the present perturbation treatment as second- and higher-order effects.

VI. DISCUSSION

Whereas the antiferromagnetic properties of nonconducting solids of 3*d* compounds at low temperatures are now considered to be relatively well understood, at least on a qualitative or semiquantitative basis, the ferromagnetic behavior of some 4*f* compounds (EuO, EuS, GdN) still presents an unsolved problem. The working hypothesis of the present paper is that the magnetic interactions in the two cases have fundamentally the same origin, and that their difference results from a different balance between a ferromagnetic and an antiferromagnetic component of the crystal energy. For the analysis, a simple model for exchange coupling between unpaired electrons in nonconducting solids has been developed on the basis of exchange perturbation theory of the Rayleigh-Schrödinger type. The exchange coupling refers to either direct cation-cation exchange or to indirect exchange via a diamagnetic anion or via the valence shells of two interacting cations. These are the first terms in a cluster expansion with regard to the number of electrons participating in magnetic coupling. The restriction to one effective magnetic electron per cation implies that we have not considered multiple-exchange interactions, i.e., contributions to the magnetic energy of the solid involving simultaneously more than one unpaired electron per cation. The number of such unpaired electrons is implicitly contained in the value of the parameter β' characterizing the orbital extension of the effective magnetic electron.

In the perturbation analysis it has been assumed that full permutation symmetry is the essential requirement to be imposed on the zeroth-order wave function for a complex *MXM* of two cations and one anion and that space-group (or point-group) symmetry is not of primary importance. This assumption implies, e.g., that the removal of degeneracy of states for an unpaired electron by the crystal field as considered in directed-orbital ligand-field theory does not play the essential role on which semiempirical rules (Goodenough-Kanamori) or more fundamental analyses are based. The results show that permutation symmetry alone *does* give rise to exchange interactions which are strongly dependent on the geometry of the complex *MXM*.

The model analyses magnetic order in nonconducting solids within the framework of a Born-Mayer type of description of ionic solids, supplemented by direct- and indirect-exchange interactions between the unpaired spins. The ions can be characterized in terms of a "diamagnetic size" (closed shells of anion and cation) and a "paramagnetic size" (open shell of cation). The values of these parameters, together with the geometries of the different complexes *MXM* (as given by the symmetry of the lattice and the lattice constant) determine the type of magnetic ordering and the transition temperature.

The magnetic order is found to result from two competitive effects, namely (direct and), superexchange interactions which, for the *B*1 structure considered, favor antiferromagnetism when summed over the crystal, and indirect exchange via the cation valence shells, which leads to ferromagnetic coupling. If the orbital of the magnetic electron is "outside" the valence shells (as for 3*d* compounds), then indirect valence-shell exchange, although not necessarily small, does not affect the stable magnetic pattern, but lowers the transition temperature. The resulting spin pattern is then predicted to be antiferromagnetic of the second kind. In the 4*f* compounds there exists a more sensitive balance between superexchange and indirect exchange via the cation valence shells, and both types of ordering (ferromagnetic and antiferromagnetic) can occur. Thus, no different models[3] for magnetic ordering need be invoked to explain differences in magnetic properties between 3*d* and 4*f* compounds, and the observed transition between ferromagnetic and antiferromagnetic behavior of Eu chalcogenides upon substituting a heavier anion, finds a ready interpretation on the basis of the present model.

Such an interpretation might not be equally obvious on the basis of configuration-interaction calculations as undertaken by Huang Liu and Orbach,[7] extended to 4*f* systems. In Sec. I we have seen that a ferromagnetic cation-cation exchange and an antiferromagnetic cation-anion-cation exchange are required to explain the experimental results for Eu chalcogenides. In the CI analysis for V^{2+} in MgO, these authors find that direct cation exchange is antiferromagnetic, whereas a strong ferromagnetic component results from indirect exchange via the anion. This is the opposite of what would be needed for 4*f* compounds.

In the present model, direct exchange between two cations, omitting the valence shells, is negligibly small both for 3*d* and 4*f* systems, whereas in the configuration-interaction analysis for 3*d* systems, such direct exchange contributes significantly to the magnetic energy. The reason for this is, apparently, that in the CI method directed orbitals are used, whereas in the present model one starts from spherically symmetric wave functions. The positive contribution to $\mathcal{J}_1$ in the model results entirely from indirect valence-shell exchange between the cations, whereas in the CI analysis there occurs a strong ferromagnetic superexchange effect. Although for 3*d* systems, in particular for V^{2+} in MgO, the final results are comparable in the two methods, the interpretation is different. Also in this respect, it would be of great interest to apply the CI method to solids with 4*f* electrons.

Contributions to the magnetic energy arising from excited states of the charge-transfer type of the complex *MXM*, as well as exchange polarization effects, occur in second and higher orders of perturbation theory. Leaving third and higher orders aside, such contributions can be dealt with parametrically in view of the similarity of first- and second-order results, the parameter being $e^2\beta/E_{\text{av}}$, with E_{av} an Unsöld energy. The value of this parameter determines whether the magnetic interactions are mainly of second or first order in perturbation theory, i.e., whether or not excited states of the complex *MXM* (for superexchange) and *MM* (for cation-cation exchange; the parameter here being $e^2\beta'/E'_{\text{av}}$) contribute significantly to the magnetic energy. On the basis of the CI analysis[7] for V^{2+} in MgO, we would conclude that second-order effects are generally smaller than those of first order. A determination of the values of the above parameters, however, goes beyond the framework of the present model. For all our numerical calculations we have considered first-order interactions only, i.e., we have assumed that neither for superexchange nor for indirect valence-shell exchange the second-order contribution is by far the larger one.

The similarity between first- and second-order energies appears to be an inherent characteristic of the exchange-perturbation theory adopted; it was also established in earlier work on crystal stability of solids with closed-shell atoms or ions.[27]

A main characteristic of the model is that the relative "size" of the orbitals for the effective electrons is an essential parameter in analyzing magnetic ordering. For this reason it is most convenient, although not necessary, to work with nodeless spherically symmetric wave functions which then are not orthogonal, neither those at the same center, nor at different centers. Orthogonalizing the orbital of the magnetic electron to that of the closed shell of the same cation does not affect the indirect-exchange energy via the valence shells. Of course, nonorthogonality between wave functions at different centers is essential in this Heitler-London type of treatment of exchange. We have recently found[28] that a model quite similar to the one employed in the present paper yields simple criteria for stability and geometric configuration of rare-gas compounds, in agreement with experiments.

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