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Exchange Interaction between Nearest-Neighbor Ion Pairs. I. V^{2+} in $KMgF_3$†

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The configuration-interaction method is applied to the exchange interaction between nearest-neighbor V^{2+} ion pairs in $KMgF_3$. A linear cation-anion-cation four-electron model is assumed, taking into account the ionic configuration as well as anion-cation and cation-cation charge-transfer excitations. Numerical estimates indicate that the charge-transfer excitation between the cations is more important than that from an anion to its neighboring cation. These two charge-transfer processes together with the ionic configuration contribute the majority of the exchange interaction. The overlap integral between two neighboring cation *d* orbitals is also taken into account, and its contributions to the exchange integral are examined and found to be significant.

I. INTRODUCTION

RECENTLY Smith and Owen[1] investigated the electron-spin-resonance spectrum of V^{2+} ion pairs in $KMgF_3$ and found the strength of exchange interaction between the nearest-neighbor V^{2+} ions to be -4.4°K (antiferromagnetic). Motivated by their measurements, we shall estimate contributions to the exchange integral arising from the following five configurations and their interactions:

A. The ionic configuration.

B. The configuration in which one electron is transferred from F^- to V^{2+} on the left.

C. The configuration in which one electron is transferred from F^- to V^{2+} on the right.

D. The configuration in which one electron is transferred from F^- to V^{2+} on the left, and at the same time an electron is transferred from V^{2+} on the right to the vacated fluorine orbital.

E. Same as D, except all transfers to the right.

The first three configurations have been investigated by Anderson,[2] Yamashita and Kondo,[3] and Keffer and Oguchi[4] for MnO, while configuration D was first considered qualitatively by Yamashita and Kondo.[3] The effects of configurations D and E are similar to the kinetic exchange suggested by Anderson.[5] This exchange is always antiferromagnetic and represents the second-order effect of virtual charge transfer between the magnetic ions. It has been suggested by Owen and Taylor[6] that the "cation-cation" transfer configurations D and E should be more important than the anion-cation transfer configurations B and C. Quantitative estimates of various contributions to the exchange interaction are difficult because of the many-electron and many-center nature of this problem and because of lack of knowledge of the response of the electronic wave functions upon charge transfer. Hence, in this paper we examine quantitatively the relative importance of the previously mentioned configurations and the sign of their contributions to the exchange interaction.

We are also interested in examining the magnitude and sign of the contributions to the exchange integral coming from the lack of orthogonality between the *d* orbitals of two V^{2+} neighbors. This overlap integral has usually been neglected in the calculations of superexchange interactions because of its small magnitude as compared to the anion-cation overlap integrals. However, we find that the cation-cation overlap integral enters in the expression for the exchange integral with lower order than the anion-cation overlap integral and thus could become important. It will turn out that the effect is numerically important for the collinear example we are treating in this paper. In the case of right-angle superexchange, to be examined in a subsequent paper, (e.g., two nearest-neighbor V^{2+} ions in MgO) the cation-cation overlap effects play an even more important (and in fact dominant) role.

We restrict ourselves to the problem of three nuclei (i.e., V-F-V) and four electrons. To fix notation, consider, in the ionic configuration, one electron occupying a d_{xz} orbital of each V^{2+} ion and two electrons in $2p_x$ orbitals of F^- ion, as shown in Fig. 1(a). All the other configurations, as well as the labeling of the orbitals are shown in Fig. 1. It is clear that because of restrictions introduced by the exclusion principle and symmetry properties, configurations D and E are allowed only in the singlet state. However, the other three configurations enter in both the singlet and triplet states. Therefore, we shall calculate the energy of the singlet state taking into account five configurations and that of the triplet state considering configurations A, B, and C only.

The wave function describing each configuration is approximated in our calculation by a single determinant

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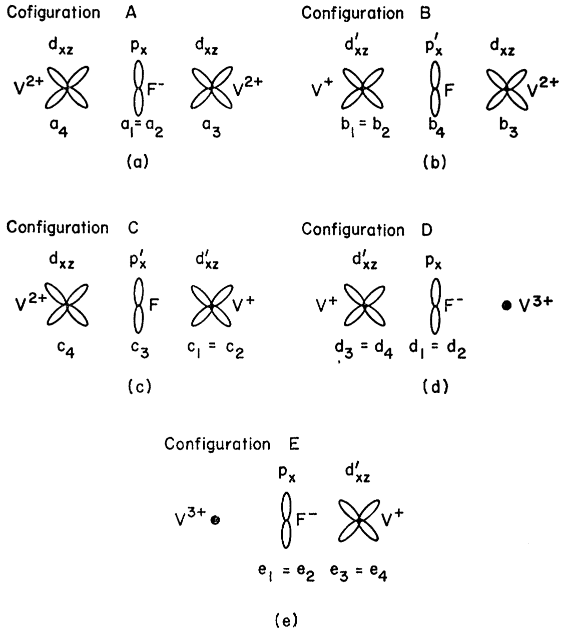

FIG. 1. Orbitals considered in a four-electron model. (a) Ionic configuration. (b) and (c) Anion-cation charge-transferred configurations. (d) and (e) Cation-cation charge-transferred configurations.

based upon the appropriate Hartree-Fock free-ion orbitals. In this approximation, the configuration interaction problem involving nonorthogonal orbitals can be solved in a relatively convenient way by using the Dirac–Van Vleck–Serber[7–9] spin-operator expansion technique. This method was first applied to the superexchange calculation by Anderson[2] and by Keffer and Oguchi.[4] The matrix element $(\mathcal{H}-W)^{R_iR_j}$ which connects R_i to R_j is given by[7]

$$(\mathcal{H}-W)^{R_iR_j}=\sqrt{2}^{\,r_i-r_j}\sum_P{}'(\mathcal{H}-W)_P{}^{R_iR_j}\mathcal{P}^{R_iR_j};\qquad (r_i\geqslant r_j),\quad (1)$$

where $\mathcal{H}$ is the sum of the total kinetic energy of the electrons, the electron-nuclear potentials, and the Coulomb interaction between electrons; W is the unknown energy in the secular equation; r_i denotes the number of pairs of filled orbitals in configuration R_i; and the summation is taken only over the $n!/2^{r_i}$ permutations which differ by more than an interchange of identical orbitals in R_i (n is the number of electrons under consideration). The coefficient $(\mathcal{H}-W)p^{R_iR_j}$ of the matrix representation of the permutation operator P is given by

$$\begin{aligned}(\mathcal{H}-W)_P{}^{R_iR_j}&=\langle P\psi^{R_i}|\mathcal{H}-W|\psi^{R_j}\rangle\\ &\equiv\mathcal{H}_P{}^{R_iR_j}-W\langle P\psi^{R_i}|\psi^{R_j}\rangle,\end{aligned}\quad (2)$$

where

$$\psi^{R_i}\equiv\varphi_1{}^i(\mathbf{r}_1)\varphi_2{}^i(\mathbf{r}_2)\cdots\varphi_n{}^i(\mathbf{r}_n)\quad (3)$$

is the product of the one-electron orbitals specifying configuration R_i. The matrix representation $\mathcal{P}^{R_iR_j}$ is determined from the physically allowed eigenstates of total spin for configurations R_i and R_j.

In the following section we shall apply (1) and (2) to calculate the matrix elements in the secular determinant for the energy of the singlet and triplet states. The exchange integral is directly related to the singlet-triplet energy separation.

II. ENERGY OF THE TRIPLET AND THE SINGLET STATE

Let us define the overlap integral between $V^{2+}(3d_{xz})$ and $F^-(2p_x)$ orbitals by

$$S=\langle a_1|a_4\rangle=-\langle a_1|a_3\rangle,\quad (4)$$

and the overlap integral between two $3d_{xz}$ orbitals centered at two nearest neighbor V^{2+} ions by

$$T=\langle a_3|a_4\rangle.\quad (5)$$

In our calculation we shall take into account the cation-cation overlap effects. Direct exchange between the vanadium ions is, therefore automatically contained in our expression for the exchange integral. These nonorthogonal effects turn out to be numerically important.

Because of restrictions imposed by symmetry properties and the exclusion principle, we note that in each configuration there is at least one pair of identical orbitals which are occupied by two electrons with opposite spin, viz., $\mathbf{s}_1$ and $\mathbf{s}_2$ form a singlet in all our configurations (cf. Fig. 1). Applying this condition and following the description for constructing matrix representation of the permutation operators given by Serber,[7] the relevant $\mathcal{P}$'s that enter in (1) are found to be

$$\mathcal{P}_I=-1;\quad \mathcal{P}_{13}=\mathcal{P}_{23}=\mathcal{P}_{14}=\mathcal{P}_{24}=-\tfrac{1}{2},\quad (6a)$$

for both the singlet and triplet states;

$$\begin{gathered}\mathcal{P}_{34}=1;\quad \mathcal{P}_{134}=\mathcal{P}_{234}=\mathcal{P}_{143}=\mathcal{P}_{243}=-\tfrac{1}{2};\\ \mathcal{P}_{13,24}=\mathcal{P}_{14,23}=1,\end{gathered}\quad (6b)$$

for the singlet state; and

$$\begin{gathered}\mathcal{P}_{34}=-1;\quad \mathcal{P}_{134}=\mathcal{P}_{234}=\mathcal{P}_{143}=\mathcal{P}_{243}=\tfrac{1}{2};\\ \mathcal{P}_{13,24}=\mathcal{P}_{14,23}=0,\end{gathered}\quad (6c)$$

for the triplet state.

A. Energy of the Singlet State

We mentioned in the previous section that configurations A, B, C, D, and E all contribute to the energy of the singlet state, hence the secular determinant is five-dimensional. Nevertheless, since the ionic configuration is even, it is connected only with even combinations of the excited configurations. Therefore,

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we form the following two even states:

$$\psi^G=(1/\sqrt{2})(\psi^B-\psi^C);\tag{7a}$$

$$\psi^{G'}=(1/\sqrt{2})(\psi^D+\psi^E).\tag{7b}$$

On substituting (3) into (7), we find

$$\psi^G=(1/\sqrt{2})[b_1(\mathbf{r}_1)b_2(\mathbf{r}_2)b_3(\mathbf{r}_3)b_4(\mathbf{r}_4)-c_1(\mathbf{r}_1)c_2(\mathbf{r}_2)c_3(\mathbf{r}_3)c_4(\mathbf{r}_4)];\tag{8a}$$

$$\psi^{G'}=(1/\sqrt{2})[d_1(\mathbf{r}_1)d_2(\mathbf{r}_2)d_3(\mathbf{r}_3)d_4(\mathbf{r}_4)+e_1(\mathbf{r}_1)e_2(\mathbf{r}_2)e_3(\mathbf{r}_3)e_4(\mathbf{r}_4)].\tag{8b}$$

Hence the 5×5 secular determinant can be factored into a 3×3 and a 2×2 part. The former contains interactions with the ground configuration and is, therefore, the only one of interest to us. It is given by

$$\begin{vmatrix}(\mathcal{H}-W)^{AA} & (\mathcal{H}-W)^{AG} & (\mathcal{H}-W)^{AG'}\\ (\mathcal{H}-W)^{GA} & (\mathcal{H}-W)^{GG} & (\mathcal{H}-W)^{GG'}\\ (\mathcal{H}-W)^{G'A} & (\mathcal{H}-W)^{G'G} & (\mathcal{H}-W)^{G'G'}\end{vmatrix}=0.\tag{9}$$

The Hamiltonian to be used here is given by

$$\mathcal{H}=\sum_i-\frac{\hbar^2}{2m}\nabla_i^2-\sum_{i,g}\frac{Z_ge^2}{r_{ig}}+\sum_{i>j}\frac{e^2}{r_{ij}},\tag{10}$$

where Z_g is the atomic number of the nucleus of the gth ion.

Observing the following equalities from symmetry considerations

$$\begin{aligned}&(\mathcal{H}-W)^{AB}=-(\mathcal{H}-W)^{AC};\quad (\mathcal{H}-W)^{AD}=(\mathcal{H}-W)^{AE};\quad (\mathcal{H}-W)^{BB}=(\mathcal{H}-W)^{CC};\\ &(\mathcal{H}-W)^{DD}=(\mathcal{H}-W)^{EE};\quad (\mathcal{H}-W)^{CD}=-(\mathcal{H}-W)^{BE};\quad (\mathcal{H}-W)^{CE}=-(\mathcal{H}-W)^{BE},\end{aligned}\tag{11}$$

and using (1) to (6b), we find the matrix elements in the secular equation to be given by

$$\begin{aligned}(\mathcal{H}-W)^{AA}=&(\mathcal{H}_I{}^{AA}-W)-(\mathcal{H}_{13}{}^{AA}-S^2W)-(\mathcal{H}_{14}{}^{AA}-S^2W)\\ &+(\mathcal{H}_{34}{}^{AA}-T^2W)-(\mathcal{H}_{134}{}^{AA}+S^2TW)-(\mathcal{H}_{143}{}^{AA}+S^2TW)+2(\mathcal{H}_{13,24}{}^{AA}-S^4W);\end{aligned}\tag{12a}$$

$$\begin{aligned}(\mathcal{H}-W)^{AG}=&\sqrt{2}(\mathcal{H}-W)^{AB}\\ =&\sqrt{2}[(\mathcal{H}_I{}^{AB}-S^3W)-(\mathcal{H}_{13}{}^{BB}+S^3TW)-(\mathcal{H}_{14}{}^{AB}-SW)\\ &+(\mathcal{H}_{34}{}^{AB}+S^3TW)-(\mathcal{H}_{134}{}^{AB}-ST^2W)-(\mathcal{H}_{143}{}^{AB}-S^3W)+2(\mathcal{H}_{13,24}{}^{AB}+STW)];\end{aligned}\tag{12b}$$

$$\begin{aligned}(\mathcal{H}-W)^{AG'}=&\sqrt{2}(\mathcal{H}-W)^{AD}\\ =&\sqrt{2}[(\mathcal{H}_I{}^{AD}-TW)-(\mathcal{H}_{13}{}^{AD}+S^2W)-(\mathcal{H}_{14}{}^{AD}-S^2TW)+(\mathcal{H}_{13,24}{}^{AD}+S^4W)];\end{aligned}\tag{12c}$$

$$\begin{aligned}(\mathcal{H}-W)^{GG}=&(\mathcal{H}-W)^{BB}-(\mathcal{H}-W)^{BC}\\ =&(\mathcal{H}_I{}^{BB}-W)-(\mathcal{H}_{13}{}^{BB}-T^2W)-(\mathcal{H}_{14}{}^{BB}-S^2W)+(\mathcal{H}_{34}{}^{BB}-S^2W)-(\mathcal{H}_{134}{}^{BB}+S^2TW)\\ &-(\mathcal{H}_{143}{}^{BB}+S^2TW)+2(\mathcal{H}_{13,24}{}^{BB}-S^2T^2W)-(\mathcal{H}_I{}^{BC}+S^2T^2W)+(\mathcal{H}_{13}{}^{BC}-S^2TW)+(\mathcal{H}_{14}{}^{BC}-S^2TW)\\ &-(\mathcal{H}_{34}{}^{BC}-T^3W)+(\mathcal{H}_{134}{}^{BC}-TW)+(\mathcal{H}_{143}{}^{BC}+S^2T^2W)-2(\mathcal{H}_{13,24}{}^{BC}+S^2W);\end{aligned}\tag{12d}$$

$$\begin{aligned}(\mathcal{H}-W)^{GG'}=&(\mathcal{H}-W)^{BD}+(\mathcal{H}-W)^{BE}\\ =&\sqrt{2}[(\mathcal{H}_I{}^{BD}-S^3TW)-(\mathcal{H}_{13}{}^{BD}+S^3W)-(\mathcal{H}_{14}{}^{BD}-STW)+(\mathcal{H}_{13,24}{}^{BD}+SW)\\ &+(\mathcal{H}_I{}^{BE}+S^3W)-(\mathcal{H}_{13}{}^{BE}-S^3TW)-(\mathcal{H}_{14}{}^{BE}-STW)+(\mathcal{H}_{13,24}{}^{BE}+ST^2W)];\end{aligned}\tag{12e}$$

$$\begin{aligned}(\mathcal{H}-W)^{G'G'}=&(\mathcal{H}-W)^{DD}+(\mathcal{H}-W)^{DE}\\ =&(\mathcal{H}_I{}^{DD}-W)-(\mathcal{H}_{13}{}^{DD}-S^2W)-(\mathcal{H}_{14}{}^{DD}-S^2W)+(\mathcal{H}_{13,24}{}^{DD}-S^4W)\\ &+(\mathcal{H}_I{}^{DE}-T^2W)-(\mathcal{H}_{13}{}^{DE}+S^2TW)-(\mathcal{H}_{14}{}^{DE}+S^2TW)+(\mathcal{H}_{13,24}{}^{DE}-S^4W).\end{aligned}\tag{12f}$$

In order to simplify the algebra involved in solving (9), we use the same procedure adopted by Keffer and Oguchi[4] of replacing W everywhere except in the term $\mathcal{H}_I{}^{AA}-W$ by its zeroth-order approximation $\mathcal{H}_I{}^{AA}$. The order of magnitude of each term in (12) is given very roughly by

$$\mathcal{H}_P{}^{R_iR_j}\simeq\text{order of }\mathcal{H}_I{}^{R_iR_i}\langle P\psi^{R_i}|\psi^{R_j}\rangle.\tag{13}$$

Taking into account only terms of order S^0, S^2, S^4, T^2, S^2T, we obtain the energy of the singlet state:

$$\begin{aligned}W_s=&\mathcal{H}_I{}^{AA}-(\mathcal{H}_{13}{}^{AA}-S^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_{14}{}^{AA}-S^2\mathcal{H}_I{}^{AA})+(\mathcal{H}_{34}{}^{AA}-T^2\mathcal{H}_I{}^{AA})\\ &-(\mathcal{H}_{134}{}^{AA}+S^2T\mathcal{H}_I{}^{AA})-(\mathcal{H}_{143}{}^{AA}+S^2T\mathcal{H}_I{}^{AA})+2(\mathcal{H}_{13,24}{}^{AA}-S^4\mathcal{H}_I{}^{AA})+2(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^{-1}\\ &\times[-(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})+2(\mathcal{H}_I{}^{AB}-S^3\mathcal{H}_I{}^{AA})-2(\mathcal{H}_{143}{}^{AB}-S^3\mathcal{H}_I{}^{AA})+4(\mathcal{H}_{13,24}{}^{AB}+ST\mathcal{H}_I{}^{AA})]\\ &-4[(\mathcal{H}_I{}^{AD}-T\mathcal{H}_I{}^{AA})-(\mathcal{H}_{13}{}^{AD}+S^2\mathcal{H}_I{}^{AA})]^2(\mathcal{H}_I{}^{DD}-\mathcal{H}_I{}^{AA})^{-1}+8(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})(\mathcal{H}_{13,24}{}^{BD}+S\mathcal{H}_I{}^{AA})\\ &\times[(\mathcal{H}_{13}{}^{AD}+S^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_I{}^{AD}-T\mathcal{H}_I{}^{AA})](\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^{-1}(\mathcal{H}_I{}^{DD}-\mathcal{H}_I{}^{AA})^{-1}+2(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})^2\\ &\times[(\mathcal{H}_{34}{}^{BB}-S^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_{14}{}^{BB}-S^2\mathcal{H}_I{}^{AA})-2(\mathcal{H}_{13,24}{}^{BC}+S^2\mathcal{H}_I{}^{AA})+(\mathcal{H}_{134}{}^{BC}-T\mathcal{H}_I{}^{AA})](\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^{-2}\\ &-4(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})^2(\mathcal{H}_{13,24}{}^{BD}+S\mathcal{H}_I{}^{AA})^2(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^{-2}(\mathcal{H}_I{}^{DD}-\mathcal{H}_I{}^{AA})^{-1}.\end{aligned}\tag{14}$$

B. Energy of the Triplet State

We only need to consider configurations A, B, and C for this case. The secular determinant is given by

$$\begin{vmatrix}(\mathcal{H}-W)^{AA} & (\mathcal{H}-W)^{AG}\\ (\mathcal{H}-W)^{GA} & (\mathcal{H}-W)^{GG}\end{vmatrix}=0. \tag{15}$$

Following the same procedures used in computing W_s except that (6c) instead of (6b) is now used, we obtain

$$\begin{aligned}(\mathcal{H}-W)^{AA}=&(\mathcal{H}_I{}^{AA}-W)-(\mathcal{H}_{13}{}^{AA}-S^2W)-(\mathcal{H}_{14}{}^{AA}-S^2W)-(\mathcal{H}_{34}{}^{AA}-T^2W)\\ &+(\mathcal{H}_{134}{}^{AA}+S^2TW)+(\mathcal{H}_{143}{}^{AA}+S^2TW);\end{aligned} \tag{16a}$$

$$\begin{aligned}(\mathcal{H}-W)^{AG}&=\sqrt{2}(\mathcal{H}-W)^{AB}\\ &=\sqrt{2}[(\mathcal{H}_I{}^{AB}-S^3W)-(\mathcal{H}_{13}{}^{AB}+S^3TW)-(\mathcal{H}_{14}{}^{AB}-SW)\\ &\quad-(\mathcal{H}_{34}{}^{AB}+S^3TW)+(\mathcal{H}_{134}{}^{AB}-ST^2W)+(\mathcal{H}_{143}{}^{AB}-S^3W)];\end{aligned} \tag{16b}$$

$$\begin{aligned}(\mathcal{H}-W)^{GG}&=(\mathcal{H}-W)^{BB}-(\mathcal{H}-W)^{BC}\\ &=(\mathcal{H}_I{}^{BB}-W)-(\mathcal{H}_{13}{}^{BB}-T^2W)-(\mathcal{H}_{14}{}^{BB}-S^2W)-(\mathcal{H}_{34}{}^{BB}-S^2W)+(\mathcal{H}_{134}{}^{BB}+S^2TW)\\ &\quad+(\mathcal{H}_{143}{}^{BB}+S^2TW)-(\mathcal{H}_I{}^{BC}+S^2T^2W)+(\mathcal{H}_{13}{}^{BC}-S^2TW)+(\mathcal{H}_{14}{}^{BC}-S^2TW)\\ &\quad+(\mathcal{H}_{34}{}^{BC}-T^3W)-(\mathcal{H}_{134}{}^{BC}-TW)-(\mathcal{H}_{143}{}^{BC}+S^2T^2W).\end{aligned} \tag{16c}$$

The energy of the triplet state is found to be

$$\begin{aligned}W_t=&\mathcal{H}_I{}^{AA}-(\mathcal{H}_{13}{}^{AA}-S^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_{14}{}^{AA}-S^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_{34}{}^{AA}-T^2\mathcal{H}_I{}^{AA})+(\mathcal{H}_{134}{}^{AA}+S^2T\mathcal{H}_I{}^{AA})+(\mathcal{H}_{143}{}^{AA}+S^2T\mathcal{H}_I{}^{AA})\\ &+2(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})[-(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})+2(\mathcal{H}_I{}^{AB}-S^3\mathcal{H}_I{}^{AA})+2(\mathcal{H}_{143}{}^{AB}-S^3\mathcal{H}_I{}^{AA})](\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^{-1}\\ &-2(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})^2[(\mathcal{H}_{14}{}^{BB}-S^2\mathcal{H}_I{}^{AA})+(\mathcal{H}_{34}{}^{BB}-S^2\mathcal{H}_I{}^{AA})+(\mathcal{H}_{134}{}^{BC}-T\mathcal{H}_I{}^{AA})](\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^{-2}.\end{aligned} \tag{17}$$

Hence, the exchange integral, defined by the coupling $-2J_{34}\mathbf{s}_3\cdot\mathbf{s}_4$ between the spins of two d electrons, is given by

$$\begin{aligned}J_{34}=&\tfrac{1}{2}(W_s-W_t)\\ =&\{(\mathcal{H}_{34}{}^{AA}-T^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_{134}{}^{AA}+S^2T\mathcal{H}_I{}^{AA})-(\mathcal{H}_{143}{}^{AA}+S^2T\mathcal{H}_I{}^{AA})+(\mathcal{H}_{13,24}{}^{AA}-S^4\mathcal{H}_I{}^{AA})\}\\ &+\left\{\frac{4(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})}{\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}}\times[-(\mathcal{H}_{143}{}^{AB}-S^3\mathcal{H}_I{}^{AA})+(\mathcal{H}_{13,24}{}^{AB}+ST\mathcal{H}_I{}^{AA})]\right.\\ &\left.+\frac{2(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})^2}{(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^2}\times[(\mathcal{H}_{34}{}^{BB}-S^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_{13,24}{}^{BC}+S^2\mathcal{H}_I{}^{AA})+(\mathcal{H}_{134}{}^{BC}-T\mathcal{H}_I{}^{AA})]\right\}\\ &+\left\{\frac{-2[(\mathcal{H}_I{}^{AD}-T\mathcal{H}_I{}^{AA})-(\mathcal{H}_{13}{}^{AD}+S^2\mathcal{H}_I{}^{AA})]^2}{\mathcal{H}_I{}^{DD}-\mathcal{H}_I{}^{AA}}\right\}\\ &+\left\{\frac{4(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})(\mathcal{H}_{13,24}{}^{BD}+S\mathcal{H}_I{}^{AA})}{(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})(\mathcal{H}_I{}^{DD}-\mathcal{H}_I{}^{AA})}\times[(\mathcal{H}_{13}{}^{AD}+S^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_I{}^{AD}-T\mathcal{H}_I{}^{AA})]\right.\\ &\left.-\frac{2(\mathcal{H}_{14}{}^{AB}-S\mathcal{H}_I{}^{AA})^2(\mathcal{H}_{13,24}{}^{BD}+S\mathcal{H}_I{}^{AA})^2}{(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^2(\mathcal{H}_I{}^{DD}-\mathcal{H}_I{}^{AA})}\right\}.\end{aligned} \tag{18}$$

For convenience we divide J_{34} in (18) into four parts:

$$J_{34}=\begin{matrix}\{J_{\text{ion}}\}\\ +\{J_{\text{ac}}\}\\ +\{J_{\text{cc}}\}\\ +\{J_{\text{ac;cc}}\}\end{matrix} \tag{19}$$

The first line in (18), denoted in (19) by J_{ion}, is the contribution to the exchange integral due to overlap effect within the ionic configuration. The second and third lines in (18), equal to J_{ac} in (19), are the effects coming from anion-cation charge transfer. Both the expressions for J_{ion} and J_{ac} agree with Keffer and Oguchi's results[4] except that we have included the effects of nonorthogonal cation orbitals. The fourth line in (18), denoted by J_{cc} in (19), comes from the cation-cation transfer and always lowers the energy of the antiferromagnetic state. The last two lines in (18), denoted by $J_{\text{ac,cc}}$ in (19), are a result of the interaction between the ionic, and the anion-cation and cation-cation transfer configurations. We notice that in (18) the terms involving the cation-cation overlap integral are of the order of T^2 and S^2T, in the sense of (13), whereas those involving the anion-cation overlap integral are of the order of S^4. Hence, it is of numerical importance to take the cation-cation overlap into account. The relative importance of the terms in (19) is estimated in the next section.

III. NUMERICAL ESTIMATES

We consider the anion-cation charge transfer energy $\mathcal{H}_I^{BB}-\mathcal{H}_I^{AA}$ entering in the denominator of (18) first. This energy is given by the sum of the following contributions: (i) the difference between the energy of an electron in $V^+(t_{2g}{}^3\uparrow,t_{2g}\downarrow)$ configuration and the ionization energy of F^- ion, (ii) the difference between the Madelung energies at the V site and the F site, (iii) the electronic polarization energy of the surrounding ions consequent upon transferring an electron from F^- to V^{2+} site, and (iv) the interaction energy between the extra electron at the V site and the "hole" at the F site. To evaluate these terms we must first examine the correlation effects arising from charge transfer. These effects are connected with the expansion of the cation d orbitals and the contraction of the anion p orbitals, as well as polarization of the neighboring ions caused by the virtual charge transfer excitation. Šimánek and Tachiki[10] pointed out that, because of the high-frequency character of this virtual excitation, charge redistribution and electronic polarization cannot be fully developed during the charge-transfer process. Hence, to a good approximation, we estimate term (i) by taking the difference between the "unoccupied" energy of V^{2+} ion[11] and the ionization energy of F^- ion. This is found to be -4.6 eV. The increase in the Madelung energy together with the electron-hole interaction energy consequent upon charge transfer is approximated by the value 26.9 eV, as found by Hubbard *et al.*[12] for a similar charge transfer process in $KNiF_3$. The electronic polarization energy is estimated by using the static formula $-\sum_i \alpha_i E_i^2$, and reduced by roughly a factor of 3 due to the dynamic effects discussed by Šimánek and Tachiki.[10] Here E_i is the electric field at the ith ion site and α_i the electronic polarizability. We consider only the anions in the immediate vicinity of the anion-cation pair involved in the charge-transfer process and use a high-frequency dielectric constant of 2 for the Coulomb interactions other than those between nearest neighbors. In this manner we find a value of -1.1 eV for the polarization energy. Summing up all the contributions, we find

$$\mathcal{H}_I^{BB}-\mathcal{H}_I^{AA}=21.2 \text{ eV}. \tag{20}$$

Next we estimate the cation-cation transfer energy $\mathcal{H}_I^{DD}-\mathcal{H}_I^{AA}$ appearing in (18), using a procedure identical to our previous one. This energy consists of (i) the difference, $\sim$21.5 eV, between the energy of V^{2+} unoccupied t_{2g} orbital and the ionization energy of V^{2+} ion, (ii) the electronic polarization energy, found to be -2.5 eV, consequent upon transferring an electron from a V^{2+} ion to its nearest V-ion neighbor, and (iii) the resulting electron-hole interaction energy of -1.8 eV. The Madelung energy is unaltered by this charge transfer. Hence we obtain

$$\mathcal{H}_I^{DD}-\mathcal{H}_I^{AA}=17.2 \text{ eV}. \tag{21}$$

To evaluate the numerators in (18) we use the V^{2+} $3d$ orbitals[11] and the F^-2p orbitals[13] computed by Watson. The one- and two-center integrals are calculated by using the modified version of the Switendick-Carbato MIDIAT program,[14] while the three-center integrals are roughly estimated by using an overlap charge model. The effects of ions other than the linear molecule V-F-V are omitted in our estimates of the numerators of (18). We find the following results:

$$S=0.0757;\quad T=-0.0018, \tag{22}$$

and

$$\begin{aligned}&\mathcal{H}_I^{AA}=-6.5787;\quad \mathcal{H}_{14}^{AB}=-0.0033;\quad \mathcal{H}_{134}^{BC}=0.0124;\quad \mathcal{H}_{134}^{AA}=-0.0001;\quad \mathcal{H}_{13,24}^{AB}=-0.0010;\\ &\mathcal{H}_{13,24}^{DB}=0.4881;\quad \mathcal{H}_{34}^{AA}<0.0001;\quad \mathcal{H}_{34}^{BB}=-0.0377;\quad \mathcal{H}_I^{DA}=0.0117;\quad \mathcal{H}_{143}^{AA}=-0.0001;\\ &\mathcal{H}_{13,24}^{BC}=0.0404;\quad \mathcal{H}_{13}^{DA}=0.0418;\quad \mathcal{H}_{13,24}^{AA}=-0.0003.\end{aligned} \tag{23}$$

Combining (18), (20), (21), (22), and (23), the various contributions to the exchange integral between two individual d electrons are found to be

$$\begin{aligned}J_{\text{ion}}&=-9.4°\text{K};\quad J_{\text{ac}}=-8.0°\text{K};\\ J_{\text{cc}}&=-16.0°\text{K};\quad J_{\text{ac,cc}}=2.1°\text{K}.\end{aligned} \tag{24}$$

Their sum gives

$$J_{34}=-31.3°\text{K}.$$

These results indicate that the cation-cation charge-transfer process contributes half of the strength of the exchange interaction, while the ionic configuration and the anion-cation transfer yield comparable contributions, but are less important as compared to the cation-cation transfer.

To determine the strength of exchange interaction $-2J_{AB}\mathbf{S}^A\cdot\mathbf{S}^B$ between the total spins S of the V^{2+} ions, we project the spin of a single electron onto the total

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spin using a method described by Van Vleck.[15] Noting that the exchange interaction for the orbitals $d_{yz}-p_y-d_{yz}$ is identical to that for $d_{xz}-p_x-d_{xz}$, we obtain

$$J_{AB}=2J_{34}/9=-7.0°\text{K}, \tag{25}$$

a result nearly two times larger than the value of -4.4°K reported by Smith and Owen.[1]

IV. DISCUSSION

We have demonstrated that the ionic configuration, together with its interactions with the anion-cation and cation-cation transfer configurations, leads to an antiferromagnetic coupling between two neighboring V^{2+} ions. In addition to these configurations, the configuration in which one electron is transferred from the anion to the neighboring cation on the left and simultaneously another electron is transferred from the anion to the cation on the right also lowers the energy of the antiferromagnetic state. We have estimated this contribution for the linear model $V^{2+}-O^{2-}-V^{2+}$ for V^{2+}:MgO and found it small compared to the contributions arising from configurations discussed in this paper. We believe that a similar situation holds for the case of V^{2+}:$KMgF_3$. Gondaira and Tanabe,[16] using orthogonalized orbitals, also found this double excitation insignificant for $KMnF_3$.

The 2s orbitals of the F^- ion play an insignificant role in the superexchange interaction, because they are orthogonal to the occupied d orbitals of V^{2+} ion. Hence, their contribution to the exchange integral is at least an order of magnitude smaller than that coming from the 2p orbitals. Moreover, charge transfer can only occur from the 2s orbitals to the e_g orbitals of the cation, which are empty and thus can be occupied by an electron with either spin direction. Hence, the importance of s-electron transfer is further reduced by roughly a factor of $J_{\text{intra}}/\Delta E\sim0.1$, where J_{intra} is the intra-atomic exchange integral between the cation d orbitals and ΔE is the separation in energy between the charge transferred configuration and the ionic configuration. The σ character of this transfer is not expected to increase its importance significantly. For the above reasons, we have not included this configuration in our estimate of the exchange integral.

It is worthwhile to point out that the lack of cation-cation orthogonality contributes 2.4°K (ferromagnetic) to J_{AB}. Of this total, 1.1°K comes from the ionic configuration and 1.3°K from the anion-cation charge transfer. It is not surprising that these effects are numerically important, because they are proportional to $T^2\sim3\times10^{-6}$ and $S^2T\sim10^{-5}$, while the anion-cation overlap effects are proportional to $S^4\sim3\times10^{-5}$. These two kinds of overlap effects are thus comparable. The cation-cation nonorthogonality will play a much more important role in the case of right-angle exchange interaction between V^{2+} ion pairs, since in this case, the largest cation-cation overlap integral is more than one third of the anion-cation overlap integral. Consequently, the anion-cation charge transfer excitation can yield a ferromagnetic coupling and the cation-cation transfer will be strongly antiferromagnetic. We shall discuss this problem in detail in a subsequent paper.

Owing to the difficulties mentioned in Sec. I, our numerical estimates of the exchange interaction between two V^{2+} ions are only necessarily semiquantitative. Similar difficulties are encountered in calculating the covalency parameters in the transition metal ion compounds.[10,12,17] It is interesting to note that whether we take into account the full correlation effect, or none at all, in estimating the transfer energies, J_{AB} only fluctuates 2°K about the value of -7°K. The relative importance of the different configurations discussed in the previous section is rather insensitive to these effects. To achieve a strictly quantitative result, we should have to consider the ions in the vicinity of the linear model V-F-V in evaluating the numerators of (18), use suitable wave functions for the d electrons of the V^+ ion in the excited configurations with intra-atomic correlation effects taken into account, and a more precise evaluation of the three-center integrals appearing in (18).

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