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Collinear Superexchange Interaction between Inequivalent Ions: V^{2+} and Ni^{2+} in MgO†

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The Dirac–Van Vleck–Serber method of configuration interaction is applied to formulate the collinear superexchange interaction between V^{2+} and Ni^{2+} ions. The major terms of the exchange integral derived by using this method are found to be equivalent to the result of Anderson's mechanism of potential exchange. The dominant contribution to the superexchange interaction is found to arise from the spin polarization of the ligand p_σ orbitals via covalent mixing with Ni^{2+} ions, in cooperation with the direct exchange between the spins of V^{2+} ions and the polarized p_σ orbitals. The strength of the interaction is computed to be 7.3°K (ferromagnetic) for V^{2+} and Ni^{2+} ions in MgO, a value which is expected to be too small by a factor of about 2. A semiempirical estimate for the exchange integral is performed for V^{2+} and Ni^{2+} ions in $KMgF_3$ by using the measured values for the unpaired spin densities in $KNiF_3$ and V^{2+}:$KMgF_3$. The strength of collinear superexchange is expected to be roughly 15°K for this case.

I. INTRODUCTION

SINCE Anderson[1] formulated Kramer's[2] idea of superexchange, numerous investigations[3] have been concentrated on the exchange interaction between identical magnetic ions in insulators. As for the case of inequivalent magnetic ions, there exist only qualitative arguments[4,5] concerning the sign of exchange coupling. In this paper we wish to study a simple case in which the magnetic orbitals of the inequivalent ions are mutually orthogonal. We choose the collinear superexchange interaction between V^{2+} and Ni^{2+} ions in MgO as an example. Consider the linear model V^{2+}—O^{2-}—Ni^{2+}. The e_g orbitals of Ni^{2+} are obviously orthogonal to the t_{2g} orbitals of V^{2+}. Qualitatively speaking, the magnetic electrons on the e_g orbitals of Ni^{2+} polarize the σ orbitals of the oxygen ion because of covalent mixing between these orbitals. This ligand σ spin density favors a ferromagnetic coupling to the spin of V^{2+} ion, since the ferromagnetic Heisenberg exchange is the only exchange interaction between orthogonal ligand σ and V^{2+} t_{2g} orbitals. This results in a ferromagnetic interaction between V^{2+} and Ni^{2+} ions because the ligand σ spin density is parallel to the spin of the Ni^{2+} ion. Similarly, the V^{2+} ion polarizes the ligand π orbitals which are coupled parallel to the spin of Ni^{2+}, again leading to a ferromagnetic interaction. In addition to the above two mechanisms, we shall also consider the mechanism in which an electron is transferred from the ligand σ orbital to the empty e_g orbital of V^{2+}. According to Hund's rule the spin of the transferred electron is energetically favorable to be parallel to that of V^{2+}. On the other hand the unpaired spin left on O^{2-} is coupled antiferromagnetically to the electron belonging to the Ni^{2+} d_{z^2} orbital, since the orbital wave functions involved here are nonorthogonal.[4] Accordingly, this mechanism also leads to a ferromagnetic interaction.

In the following section we shall use the Dirac–Van Vleck–Serber method of configuration interaction[6–8] to calculate the spin-dependent part of the ground-state energy, allowing for admixture of charge-transfer excitations into the ionic configuration. This method has been applied in our previous calculations for the exchange interaction between nearest-neighbor V^{2+} ions in $KMgF_3$[9] and in MgO.[10] For the present case, where the magnetic orbitals are orthogonal, we expect Anderson's mechanism of "potential exchange"[3] to contribute the majority of exchange interaction. We shall, in fact, relate the numerically important terms in our expression for the exchange integral to the result of potential exchange. Thus, to a good approximation, the strength of exchange interaction may be estimated from the values of the measured covalency parameters and some two-electron integrals. In Sec. III an attempt is made to estimate the exchange integral between V^{2+} and Ni^{2+} ions in MgO. The difficulties involved in performing such a numerical evaluation have been discussed in Refs. 9 and 10. Since the unpaired spin densities in the ligand orbitals are known for $KNiF_3$[11] and V^{2+}:$KMgF_3$,[12] we shall use these values to estimate semiempirically the exchange interaction between Ni^{2+} and V^{2+} ions in $KMgF_3$.

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II. EXPRESSION FOR THE EXCHANGE INTEGRAL

Following the approximations that we adopted in our previous calculations,[9,10] we consider a four-electron, three-center model. Polarization of the ligand σ and π orbitals are treated separately in the following.

A. Superexchange via Ligand σ Orbitals

For the ionic configuration A, we consider the following orbitals: Ni^{2+} $3d_{z^2}$, O^{2-} $2p_z(\uparrow)$ $2p_z(\downarrow)$, and V^{2+} $3d_{xz}$. The excited configurations to be considered in this paper are configuration B in which an electron is transferred from the $2p_z$ orbital to the neighboring empty e_g orbital of the V^{2+} ion, and configuration C in which an electron is transferred from the p_z orbital to the half-filled d_{z^2} orbital of the Ni^{2+} ion. These configurations (and the labeling of the one-electron orbitals involved) are shown in Fig. 1. We expect configuration B to be of less numerical importance as compared to configuration C, owing to the fact that an electron with its spin either parallel or antiparallel to the spins of a V^{2+} ion is allowed to occupy the e_g orbital of V^{2+}. As a result, the net strength of the superexchange interaction is reduced. For the same reason we neglect the excitation of transferring an electron from the Ni^{2+} $3d_{z^2}$ orbital to the empty $3d_{z^2}$ orbital of V^{2+}. The validity of this approximation is further supported by the fact that the anion $2p_z$ orbital is an odd function while the $2s$ orbital is even, thus leading to a partial cancellation between contributions to the cation → cation charge-transfer integral via the $2p$ and $2s$ orbitals. A detailed calculation which demonstrates this type of cancellation has been given in estimating the $3d\rightarrow 4s$ charge-transfer integral between two Mn^{2+} ions in $\mathrm{KMgF_3}$ and MnO.[13]

The matrix element which connects the ith configuration with the jth has been derived by Serber.[8] It is given by

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

where $\mathcal{H}$ is the Hamiltonian for the electrostatic interactions between electrons, the electron-nuclear attractions, and the electronic kinetic energies, W is the unknown eigenvalue to be solved by setting up the secular determinant, r_i is the number of pairs of filled orbitals in configuration R_i, and the sum is carried over the $\frac{1}{2}n!$ permutations which differ by more than an interchange of identical orbitals in R_i (n = number of electrons under consideration). The coefficient of the matrix representation of the permutation operator, $\mathcal{P}^{R_iR_j}$, is given by the expression

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

where

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

is the product of the one-electron orbitals characterizing configuration R_i. Construction of the $\mathcal{P}^{R_iR_j}$'s was demonstrated in our previous work on the exchange between nearest V^{2+} ion pairs in $\mathrm{KMgF_3}$ and in MgO[9,10]. In the latter problem we have considered configurations similar to configurations A, B, and C in the present case. Namely, in these configurations the anion orbital under consideration is orthogonal to one neighboring cation orbital but overlaps with the other cation orbital (see Sec. IIIA in Ref. 10). Modifying our previous result [Eq. (14) in Ref. 10] slightly by taking into account the facts that for the present case (i) the cation orbitals are mutually orthogonal and (ii) only the p_σ orbital is taken into account, we obtain the following expression for the major terms in the superexchange interaction via the p_σ orbital:

$$\begin{aligned}J^\sigma=\mathcal{H}_{13,24}{}^{AA}&-\frac{2(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\sigma')}{\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA}}\mathcal{H}_{134}{}^{AC}\\
&+\frac{(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\sigma')^2}{(\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA})^2}\mathcal{H}_{34}{}^{CC}+\mathcal{H}_{34}{}^{AA}-2\mathcal{H}_{134}{}^{AA}\\
&+\frac{2(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\sigma')}{\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA}}\mathcal{H}_{13,24}{}^{AC}\\
&-\frac{2(\mathcal{H}_I{}^{AB}-\mathcal{H}_I{}^{AA}S_\sigma)}{\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}}\mathcal{H}_{14,23}{}^{AB}\\
&+\frac{(\mathcal{H}_I{}^{AB}-\mathcal{H}_I{}^{AA}S_\sigma)^2}{(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^2}\mathcal{H}_{14,23}{}^{BB}\\
&+\frac{2(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\sigma')(\mathcal{H}_I{}^{AB}-\mathcal{H}_I{}^{AA}S_\sigma)}{(\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA})(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})}\mathcal{H}_{134}{}^{BC},\end{aligned} \tag{4}$$

where the overlap integrals S_σ and S_σ' are defined by

$$\begin{aligned}S_\sigma&=\langle 2p_z(\mathrm{O}^{2-})\,|\,3d_{z^2}(\mathrm{V}^{2+})\rangle,\\ S_\sigma'&=\langle 2p_z(\mathrm{O}^{2-})\,|\,3d_{z^2}(\mathrm{Ni}^{2+})\rangle.\end{aligned} \tag{5}$$

The explicit expressions for the matrix elements entering in the numerators of (4) can be calculated by using (2) and (3). They are given in the Appendix. Observing Eq. (A2), we can identify $(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\sigma')\times(\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA})^{-1}$ as the charge-transfer parameter B_σ between $2p_z$ and the empty $3d_{z^2}$ of Ni^{2+}. Substituting (A1), (A3) and (A4) into (4), the first three terms for J^σ reduce to the simpler form

$$\begin{aligned}\mathcal{H}_{13,24}{}^{AA}&-\frac{2(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\sigma')}{\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA}}\mathcal{H}_{134}{}^{AC}\\
&+\frac{(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\sigma')^2}{(\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA})^2}\mathcal{H}_{34}{}^{CC}\\
&=f_\sigma(\mathrm{Ni})\langle d_{xz}(\mathrm{V}^{2+})p_z\,|\,e^2/r_{ij}\,|\,p_zd_{xz}(\mathrm{V}^{2+})\rangle,\end{aligned} \tag{6}$$

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[13] Nai Li Huang, R. Orbach, E. Šimánek, J. Owen, and D. R. Taylor, Phys. Rev. **156**, 283 (1967).

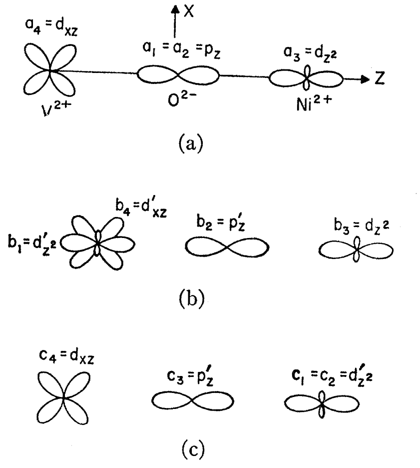

FIG. 1. (a) Ionic configuration A considered in the superexchange interaction via p_z orbitals. (b) Configuration B in which an electron is transferred from O^{2-} p_z to the empty d_{z^2} orbital of V^{2+}. (c) Configuration C in which an electron is transferred from O^{2-} p_z to the half-filled d_{z^2} orbital of Ni^{2+}.

where

$$f_\sigma(\mathrm{Ni}) = \left(\frac{\mathcal{H}_{13}{}^{AC} - \mathcal{H}_I{}^{AA} S_\sigma'}{\mathcal{H}_I{}^{AA} - \mathcal{H}_I{}^{CC}} + S_\sigma'\right)^2$$
$$\equiv (B_\sigma + S_\sigma')^2 \tag{7}$$

is the unpaired spin density in the $2p_\sigma$ orbitals arising from the covalent mixing with the Ni^{2+} $3d_{z^2}$ orbital. Equation (6) represents the Heisenberg exchange between V^{2+} $3d_{xz}$ and the unpaired spin density $f_\sigma(\mathrm{Ni})$, in agreement with our qualitative arguments given in the previous section. It is of interest to note that the contributions to J^σ due to configurations A and C can be expressed by the following simple form:

$$J_{A,C}{}^\sigma = \langle [d_{z^2}(\mathrm{Ni}^{2+}) - A_\sigma p_z] d_{xz}(\mathrm{V}^{2+}) \mid e^2/r_{ij} \mid d_{xz}(\mathrm{V}^{2+}) \times [d_{z^2}(\mathrm{Ni}^{2+}) - A_\sigma p_z] \rangle, \tag{8}$$

where $A_\sigma \equiv B_\sigma + S_\sigma'$. Equation (8) obviously corresponds to the direct exchange between $d_{xz}(V^{2+})$ and the antibonding molecular orbital $[d_{z^2}(Ni^{2+}) - A_\sigma p_z]$ and is necessarily ferromagnetic.[14] Numerical estimates will show that this direct-exchange interaction contributes the majority of J^σ.

B. Superexchanhe via Ligand π Orbitals

In the ionic configuration α, we consider the following orbitals: V^{2+} $3d_{xz}$, O^{2-} $2p_x(\uparrow)2p_x(\downarrow)$ and Ni^{2+} $3d_{z^2}$, as shown in Fig. 2(a). Since the orbitals $2p_x$ and Ni^{2+} $3d_{z^2}$ are orthogonal, no charge transfer between these orbitals can occur. The only allowed excited configuration, denoted by γ, corresponds to the transferring of an electron from oxygen $2p_x$ to the unoccupied $3d_{xz}$ orbital of V^{2+} as shown in Fig. 2(b). Clearly, the present case is parallel to configurations A and C that we just discussed. We define the overlap integral

$$S_\pi = \langle 2p_x(\mathrm{O}^{2-}) \mid 3d_{xz}(\mathrm{V}^{2+}) \rangle. \tag{9}$$

The exchange integral via $2p_\pi$ orbitals can be immediately obtained from (4) by changing A to α, C to γ, and S_σ' to S_π. We find

$$J^\pi = \mathcal{H}_{13,24}{}^{\alpha\alpha} - \frac{2(\mathcal{H}_{13}{}^{\alpha\alpha} - \mathcal{H}_I{}^{\alpha\alpha} S_\pi)}{\mathcal{H}_I{}^{\gamma\gamma} - \mathcal{H}_I{}^{\alpha\alpha}} \mathcal{H}_{134}{}^{\alpha\gamma} + \frac{(\mathcal{H}_{13}{}^{\alpha\gamma} - \mathcal{H}_I{}^{\alpha\alpha} S_\pi)^2}{(\mathcal{H}_I{}^{\gamma\gamma} - \mathcal{H}_I{}^{\alpha\alpha})^2} \mathcal{H}_{34}{}^{\gamma\gamma} + \mathcal{H}_{34}{}^{\alpha\alpha} - 2\mathcal{H}_{134}{}^{\alpha\alpha} + \frac{2(\mathcal{H}_{13}{}^{\alpha\gamma} - \mathcal{H}_I{}^{\alpha\alpha} S_\pi)}{\mathcal{H}_I{}^{\gamma\gamma} - \mathcal{H}_I{}^{\alpha\alpha}} \mathcal{H}_{13,24}{}^{\alpha\gamma}, \tag{10}$$

in which the matrix elements are expressed in terms of the one-electron and two-electron integrals by (A1)–(A7) with S_σ' and the one-electron orbitals a_1, a_2, a_3, and a_4 (labeled in Fig. 1) to be replaced by S_π, α_1, α_2, α_3, and α_4 (labeled in Fig. 2), respectively. In analogy to (8), we can rewrite (6) as the direct exchange between $d_{z^2}(Ni^{2+})$ and the antibonding π orbital $[d_{xz}(V^{2+}) - A_\pi p_x]$:

$$J^\pi = \langle [d_{xz}(\mathrm{V}^{2+}) - A_\pi p_x] d_{z^2}(\mathrm{Ni}^{2+}) \mid e^2/r_{ij} \mid d_{z^2}(\mathrm{Ni}^{2+}) \times [d_{xz}(\mathrm{V}^{2+}) - A_\pi p_x] \rangle, \tag{10}$$

where

$$A_\pi = \frac{\mathcal{H}_{13}{}^{\alpha\gamma} - \mathcal{H}_I{}^{\alpha\alpha} S_\pi}{\mathcal{H}_I{}^{\alpha\alpha} - \mathcal{H}_I{}^{\gamma\gamma}} + S_\pi. \tag{11}$$

We note that the sign of J^π is also necessarily ferromagnetic.[14]

In our above treatment, contributions to the superexchange interaction via oxygen $2p_\sigma$ and $2p_\pi$ orbitals have been considered separately for the purpose of convenience. As a result, the exchange integrals $J_{A,C}{}^\sigma$ and J^π represent the direct exchange between the antibonding molecule orbital at one magnetic ion site and the atomic orbital at the other. However, to be more precise one should obviously consider the direct-

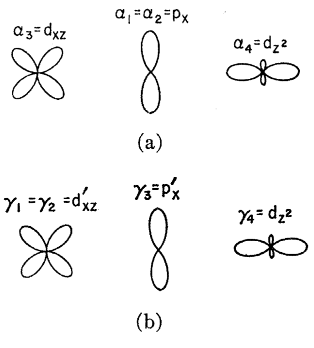

FIG. 2. (a) Ionic configuration α considered in the superexchange interaction via p_x orbitals. (b) Configuration γ in which an electron is transferred from O^{2-} p_x to the half-filled d_{xz} orbital of V^{2+}.

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[14] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I, p. 486.

exchange interaction between *both* molecular orbitals $[d_{xz}(\mathrm{V}^{2+})-A_\pi p_x]$ and $[d_{z^2}(\mathrm{Ni}^{2+})-A_\sigma p_z]$. This is the potential-exchange interaction discussed by Anderson.[3] For the present problem, the potential-exchange integral can be written as

$$J_{\mathrm{pot}}=\langle[d_{xz}(\mathrm{V}^{2+})-A_\pi p_x][d_{z^2}(\mathrm{Ni}^{2+})-A_\sigma p_z]\,|\,e^2/r_{ij}\,|\times[d_{z^2}(\mathrm{Ni}^{2+})-A_\sigma p_z][d_{xz}(\mathrm{V}^{2+})-A_\pi p_x]\rangle. \quad (12)$$

We note that the major terms in (12) are given by the sum of $J_{A,C}{}^\sigma$ and J^π. [In principle, direct exchange between $d_{xz}(\mathrm{V}^{2+})$ and $d_{z^2}(\mathrm{Ni}^{2+})$ orbitals should be taken into account only once in forming the sum, $J_{A,C}{}^\sigma+J^\pi$, although this term is found to be numerically unimportant.] This demonstrates that, for the exchange interaction between orthogonal magnetic orbitals, the method of configuration interaction leads to a result in agreement with Anderson's mechanism of potential exchange to the order that we work with. The relative importance of $J_{A,C}{}^\sigma$ and J^π clearly depends on the values of A_σ and A_π, and also on the magnitudes of the direct-exchange integrals

$$\langle d_{xz}(\mathrm{V}^{2+})p_z\,|\,e^2/r_{ij}\,|\,p_z d_{xz}(\mathrm{V}^{2+})\rangle$$

and

$$\langle d_{z^2}(\mathrm{Ni}^{2+})p_x\,|\,e^2/r_{ij}\,|\,p_x d_{z^2}(\mathrm{Ni}^{2+})\rangle.$$

Numerical estimates, to be performed in the next section, demonstrate that the direct-exchange integral between p_x and $d_{z^2}(\mathrm{Ni}^{2+})$ is much smaller than that between p_z and $d_{xz}(\mathrm{V}^{2+})$, probably owing to the fact that the radial wave function of the Ni^{2+} $3d$ orbital is less extended as compared to the V^{2+} $3d$ orbital. Hence, $J_{A,C}{}^\sigma$ contributes the majority of the potential exchange. It should be mentioned that we are unable to relate our *entire* expression for J^σ, i.e., Eq. (4), to Anderson's mechanisms. The difficulty arises from the fact that the introduction of configuration B (i.e., the transferring of an electron from O^{2-} to the empty e_g orbital of V^{2+}) not only complicates the formulation of the potential exchange, but also allows for Anderson's mechanism of kinetic exchange[3] to enter. However, for the present problem, numerical estimates indicate that configuration B contributes only a minor part of J^σ, as compared with the direct-exchange interaction between the d_{xz} (and d_{yz}) orbital of V^{2+} and the ligand p_z orbital which is spin polarized via overlap and covalent mixing with Ni^{2+} d_{z^2}. Nevertheless, it should be pointed out that charge transfer from the ligand to the empty e_g orbital of a neighboring magnetic ion is responsible for some observed properties. For example, in chromium-nitrosyl complexes Danon *et al.*[15] explained their measured ligand hyperfine interactions on the basis of such charge-transfer excitations. Also, Owen and Taylor[16] have measured the hyperfine interaction with the Al nucleus in Cr^{3+}:$\mathrm{LaAlO_3}$ by using the ENDOR technique. They have shown that the hyperfine constants A_s and A_σ can be attributed to the overlap between aluminum $2s$ and the spin-polarized oxygen $2s$ and $2p_\sigma$ orbitals (also to the charge transfer from ligand to the empty aluminum $3s$ orbital). The unpaired ligand spin densities, again, arise from charge transfer to the empty $\mathrm{Cr}^{3+}3d(e_g)$ or $4s$ orbital.

III. NUMERICAL ESTIMATES

Evaluation of the exchange integrals J^σ and J^π are performed in a manner identical to our previous computations for the exchange interaction between a pair of V^{2+} ions in $\mathrm{KMgF_3}$ and MgO.[9,10] Values for the one-electron and two-electron integrals entered in (4) and (10) are listed in Tables I and II. The transfer energies $\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}$, $\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA}$, and $\mathcal{H}_I{}^{\gamma\gamma}-\mathcal{H}_I{}^{\alpha\alpha}$ correspond, respectively, to the energy required in transferring an electron from O^{2-} p_σ to the empty d_{z^2} orbital of V^{2+}, from O^{2-} $2p_\sigma$ to Ni^{2+} d_{z^2}, and from O^{2-} p_π to V^{2+} d_{xz}. The procedures for estimating these transfer energies have been discussed in detail in our previous work.[9,10] For the present case we find

$$\begin{aligned}\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}&=0.59\text{ a.u.},\\ \mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA}&=0.60\text{ a.u.},\\ \mathcal{H}_I{}^{\gamma\gamma}-\mathcal{H}_I{}^{\alpha\alpha}&=0.69\text{ a.u.}\end{aligned} \quad (13)$$

Substituting (13) and the values listed in Tables I and II into (4) and (10), we obtain

$$J^\sigma=19.8°\mathrm{K}; \quad (14a)$$

$$J^\pi=0.5°\mathrm{K}. \quad (14b)$$

In arriving at these results, it is found that the direct exchange between $d_{xz}(\mathrm{V}^{2+})$ and $[d_{z^2}(\mathrm{Ni}^{2+})-A_\sigma p_z]$, i.e., the exchange integral $J_{A,C}{}^\sigma$ given by (8), contributes 15.8°K to J^σ.[17] Thus configuration B, discussed in Sec. IIA, yields a minor contribution (i.e., 4°K) to J^σ as compared with configurations A and C. The sign of J^σ and J^π indicates that the superexchange interaction via oxygen p_z and p_x orbitals are both ferromagnetic, as we expected. However, the contribution via p_x orbital (J^π) is found to be much smaller than that via p_z orbital (J^σ). This is caused by the fact that the direct-exchange integral $\langle\phi_i\phi_j\,|\,e^2/r_{12}\,|\,\phi_j\phi_i\rangle$ between p_x and $d_{z^2}(\mathrm{Ni}^{2+})$ orbitals is found to be 0.00016 a.u., whereas the same integral between p_z and $d_{xz}(\mathrm{V}^{2+})$ orbitals has a value of 0.00360 a.u. The sum of (14a) and (14b) yields a value of 20.3°K for the superexchange interaction between $d_{xz}(\mathrm{V}^{2+})$ and $d_{z^2}(\mathrm{Ni}^{2+})$ orbitals.

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[15] J. Danon, H. Panepucci, and A. A. Misetich, J. Chem. Phys. **44**, 4154 (1966).

[16] J. Owen and D. R. Taylor (private communication).

[17] In evaluating J^σ, we have omitted the three-center integral $\langle a_4a_1\,||\,a_3a_4\rangle$ because we are unable to make an estimate. However, we believe that this integral is more than an order of magnitude less than the direct-exchange integral $\langle a_4a_1\,||\,a_1a_4\rangle$, since it involves the charge density $a_4{}^*a_3$ of two well-separated orthogonal orbitals. Hence the major term in (8) is given by (6).

TABLE I. One-electron integrals and two-electron integrals entered in (A1)–(A11) and the resulting matrix elements for (4). The values are given in atomic units. The overlap integrals S_σ and S_σ' defined by (5) are also listed. The one-electron orbitals a_i are labeled in Fig. 1.

$\langle a_1a_1 \| a_1a_1\rangle = 0.63901$
$\langle a_4a_1 \| a_1a_4\rangle = 0.00360$
$\langle a_3a_1 \| a_3a_3\rangle = 0.03733$
$\langle a_1a_1 \| a_3a_1\rangle = 0.03573$
$\langle a_1a_3 \| a_1a_3\rangle = 0.24876$
$\langle a_1a_4 \| a_1a_4\rangle = 0.27035$
$\langle a_1a_1 \| b_1a_1\rangle = -0.06283$
$\langle a_1a_4 \| b_1a_4\rangle = -0.04996$
$\langle a_4a_1 \| b_1a_4\rangle = -0.00379$
$\langle a_4b_1 \| b_1a_4\rangle = 0.02100$
$\langle a_1a_4 \| a_3a_4\rangle \simeq 0.01$
$\langle a_1a_3 \| b_1a_3\rangle \simeq -0.009$
$\langle a_4a_1 \| a_3a_4\rangle^{\mathrm{a}}$
$S_\sigma = \langle a_1 | b_1\rangle = -0.10425$
$S_\sigma' = \langle a_1 | a_3\rangle = 0.06162$
$\langle a_1 | \mathcal{H}_1 | a_1\rangle = -2.34310$
$\langle a_1 | \mathcal{H}_1 | b_1\rangle = 0.37821$
$\langle a_1 | \mathcal{H}_1 | a_3\rangle = -0.18956$
$\mathcal{H}_{13,24}{}^{AA} = 0.00001$
$\mathcal{H}_{13}{}^{AC} - S_\sigma'\mathcal{H}_I{}^{AA} = -0.03357$
$\mathcal{H}_I{}^{AB} - S_\sigma\mathcal{H}_I{}^{AA} = 0.13284$
$\mathcal{H}_{134}{}^{AC} = 0.00022$
$\mathcal{H}_{14,23}{}^{AB} = -0.00001$
$\mathcal{H}_{34}{}^{CC} = 0.00360$
$\mathcal{H}_{134}{}^{BC} = -0.00023$
$\mathcal{H}_{14,23}{}^{BB} = 0.00008$

[a] We are unable to estimate this matrix element and have ignored it in the computation of J^σ.

In addition to the exchange interaction between $d_{xz}(\mathrm{V}^{2+})$ and $d_{z^2}(\mathrm{Ni}^{2+})$ orbitals, interactions between the following orbitals also contribute to the exchange coupling energy between the spins of V^{2+} and Ni^{2+} ions:

(i) $d_{yz}(\mathrm{V}^{2+})$—p_y and $p_z(\mathrm{O}^{2-})$—$d_{z^2}(\mathrm{Ni}^{2+})$.

This case is identical to the interaction between $d_{xz}(\mathrm{V}^{2+})$ and $d_{z^2}(\mathrm{Ni}^{2+})$ orbitals because of axial symmetry about the z axis. Thus the strength of superexchange coupling is also 20.3°K.

(ii) $d_{xy}(\mathrm{V}^{2+})$—$p_z(\mathrm{O}^{2-})$—$d_{z^2}(\mathrm{Ni}^{2+})$.

The superexchange integral for this case is identical in form to (4). Following the procedures adopted in evaluating (14), we find the strength of this interaction to be 3.4°K. This value is considerably smaller than the exchange integral of 20.3°K between $d_{xz}(\mathrm{V}^{2+})$ and $d_{z^2}(\mathrm{Ni}^{2+})$ orbitals, because the charge distribution of $d_{xy}(\mathrm{V}^{2+})$ is concentrated in a plane (xy plane) perpendicular to the line joining the ions (the z axis), whereas the $d_{xz}(\mathrm{V}^{2+})$ orbital is in the xz plane. Consequently, the direct-exchange interaction between $d_{xy}(\mathrm{V}^{2+})$ and $p_z(\mathrm{O}^{2-})$ orbitals is much weaker as compared to the corresponding interaction between $d_{xz}(\mathrm{V}^{2+})$ and $p_z(\mathrm{O}^{2-})$ orbitals.

(iii) $d_{xz}(\mathrm{V}^{2+})$—$p_x(\mathrm{O}^{2-})$—$d_{x^2-y^2}(\mathrm{Ni}^{2+})$,

or

$d_{yz}(\mathrm{V}^{2+})$—$p_y(\mathrm{O}^{2-})$—$d_{x^2-y^2}(\mathrm{Ni}^{2+})$.

The exchange interaction is caused by a mechanism identical to that for J^π. However, for the present case, direct exchange between $d_{x^2-y^2}(\mathrm{Ni}^{2+})$ and p_x(or p_y) orbitals is found to be 7×10^{-5} a.u., a value much too small to yield any significant contribution to the superexchange. Therefore, we shall neglect this case.

We list in the following our previously discussed major superexchange interactions:

$$\begin{array}{lllc}
\multicolumn{3}{c}{\mathrm{V}^{2+}\text{—}\mathrm{O}^{2}\text{—}\mathrm{Ni}^{2+}} & \begin{array}{c}\text{Strength of interaction}\\ (°\mathrm{K})\end{array} \\
d_{xz} & p_z \text{ and } p_x & d_{z^2} & 20.3 \\
d_{yz} & p_z \text{ and } p_y & d_{z^2} & 20.3 \\
d_{xy} & p_z & d_{z^2} & 3.4.
\end{array} \tag{15}$$

The exchange integral J_{AB} between the spins of V^{2+} and Ni^{2+} ions is related to the sum of the exchange integral J_{ij} between two individual d electrons by the expression derived by Van Vleck,[18]

$$J_{AB} = (n_An_B)^{-1} \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} J_{ij}, \tag{16}$$

where $n_A=3$ for V^{2+} and $n_B=2$ for Ni^{2+}. Substituting (15) into (16), we find

$$J_{AB} = 7.3°\mathrm{K}, \tag{17}$$

for the exchange integral entering in the exchange interaction $-2J_{AB}\mathbf{S}(\mathrm{V}^{2+})\cdot\mathbf{S}(\mathrm{Ni}^{2+})$.

It is of interest to point out that from Tables I and II, and Eqs. (7) and (11), the unpaired oxygen spin

TABLE II. One-electron integrals, two-electron integrals, and the matrix elements in (10) in atomic units. The overlap integral defined by (9) is also given. The one-electron orbitals α_i are shown in Fig. 2.

$\langle \alpha_3\alpha_1 \| \alpha_3\alpha_3\rangle = 0.03171$
$\langle \alpha_1\alpha_1 \| \alpha_3\alpha_1\rangle = 0.03418$
$\langle \alpha_4\alpha_1 \| \alpha_1\alpha_4\rangle = 0.00016$
$\langle \alpha_1\alpha_1 \| \alpha_1\alpha_1\rangle = 0.63901$
$\langle \alpha_1\alpha_3 \| \alpha_1\alpha_3\rangle = 0.24371$
$\langle \alpha_1\alpha_4 \| \alpha_1\alpha_4\rangle = 0.22122$
$\langle \alpha_1\alpha_4 \| \alpha_3\alpha_4\rangle \simeq 0.01$
$\langle \alpha_3\alpha_4 \| \alpha_4\alpha_3\rangle \simeq 10^{-8}$
$\langle \alpha\alpha \| \alpha\alpha\rangle^{\mathrm{a}}$
$\langle \alpha_1 | \mathcal{H}_1 | \alpha_1\rangle = -2.34310$
$\langle \alpha_1 | \mathcal{H}_1 | \alpha_3\rangle = -0.19206$
$S_\pi = \langle \alpha_1 | \alpha_3\rangle = 0.08202$
$\mathcal{H}_{13,24}{}^{AA} < 0.00001$
$\mathcal{H}_{13}{}^{AC} - S_\pi\mathcal{H}_I{}^{AA} = -0.01433$
$\mathcal{H}_{134}{}^{AC} = 0.00001$
$\mathcal{H}_{34}{}^{CC} = 0.00016$

[a] We are unable to estimate this matrix element and have ignored it in the computation of J^π.

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[18] J. H. Van Vleck, Rev. Univ. Nacl. Tucuman, Ser. A **14**, 189 (1962).

densities f_σ and f_π are found to be 1.4 and 1.7%, respectively. For V^{2+}:$KMgF_3$, Hall *et al.*[12] observed a value of 4.15% for $f_\pi - f_\sigma$ in $F-2p$ orbitals. Since for this case the unpaired spin density f_σ in $2p_\sigma$ orbitals has a small and negative value, the unpaired spin density f_π in $2p_\pi$ is then slightly smaller than 4.15%. For the V^{2+}—O^{2-} bond in MgO, it seems reasonable to expect roughly a value of 4% for f_π. Therefore, we believe that our estimate for f_π (and also for f_σ) is at least a factor of 2 too small. In other words, we expect the strength of interaction between V^{2+} and Ni^{2+} ions in MgO to be around 15°K. Up to now, no experiment has been performed to measure the superexchange interaction for this case. However, for La_2NiMnO_6, Blasse[19] determined the charge distribution to be Ni^{2+} and Mn^{4+} (Mn^{4+} and V^{2+} have isoelectronic structures) and observed a strongly ferromagnetic collinear exchange interaction between Ni^{2+} and Mn^{4+} ions. Using his measured value for the Curie temperature and a simple molecular-field approximation, we deduce a value of 27°K for the collinear exchange integral between V^{2+} and Mn^{4+} ions. This value is considerably larger than our expected value for V^{2+}, Ni^{2+}:MgO, possibly because of the stronger covalency between Mn^{4+} and O^{2-} ions, as compared to that between V^{2+} and O^{2-} ions and also because of the smaller lattice constant for La_2NiMnO_6 in comparison with that for MgO.

IV. CONCLUSION AND DISCUSSION

We have demonstrated that the collinear superexchange interaction between a pair of V^{2+} and Ni^{2+} ions in MgO is ferromagnetic and has a strength of 7.3°K. For this particular case where the orbitals of two magnetic ions are orthogonal, we have shown that Anderson's mechanism of potential exchange yields a result to be equivalent to the major terms obtained by using the Dirac–Van Vleck–Serber method of configuration interaction. The dominant contribution to the exchange interaction is found to be the direct exchange between the antibonding orbital $[d_{z^2}(Ni^{2+}) - A_\sigma p_\sigma]$ and the d_{xz} (or d_{yz}) orbital of a V^{2+} ion.

A strict quantitative calculation for the exchange integral is very difficult to achieve[9,10] because of the charge-redistribution and lattice-polarization effects. In addition, there are computational difficulties regarding evaluation of the three-center integrals and contributions of the crystal surroundings to the matrix elements (A1)–(A11). However, in spite of these difficulties, a semiempirical estimate for the exchange integral can be performed by using (12) if the covalency parameters A_σ and A_π are known. The collinear superexchange interaction between V^{2+} and Ni^{2+} ions in $KMgF_3$ can be approximately computed in this manner. We take the measured value of 3.78% for $f_\sigma(=A_\sigma^2)$ in $KNiF_3$,[11] and roughly 4% for $f_\pi(=A_\pi^2)$ in V^{2+}:$KMgF_3$.[12] From (8), (10), and (16) we find the strength of the superexchange interaction to be roughly 15°K, a result yet to be confirmed by experiments.

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APPENDIX

The matrix elements entering (4) can be written in terms of the one-electron and two-electron integrals by the following procedures. Consider the spin-independent Hamiltonian

$$\mathcal{H} = \sum_i \mathcal{H}_i + \sum_{i>j} e^2/r_{ij},$$

with

$$\mathcal{H}_1 = (-\hbar^2/2m)\nabla_1^2 + V(V^{3+}) + V(Ni^{3+}) + V(O).$$

Here $V(V^{3+})$, $V(Ni^{3+})$, and $V(O)$ are the effective one-electron potential energies arising from the V^{3+} ion, the Ni^{3+} ion, and the O atom, respectively. The ionicities have been chosen in the above manner so that the interaction between the four electrons under consideration are not included again in $\mathcal{H}$. Using (2), (3), and the approximation[9,10,13] of replacing the one-electron orbitals b_2, c_3 by a_1 and c_1, b_3 by a_3, etc., and defining $\langle\phi_1\phi_2 | e^2/r_{ij} | \phi_3\phi_4\rangle \equiv \langle\phi_1\phi_2 \| \phi_3\phi_4\rangle$, we obtain

$$\mathcal{H}_{13,24}{}^{AA} = \langle a_4a_1 \| a_1a_4\rangle S_\sigma'^2, \tag{A1}$$

$$\begin{aligned}\mathcal{H}_{13}{}^{AC} - \mathcal{H}_I{}^{AA}S_\sigma' = {} & \langle a_1 | \mathcal{H}_1 | a_3\rangle - \langle a_1 | \mathcal{H}_1 | a_1\rangle S_\sigma' \\ & + \langle a_3a_1 \| a_3a_3\rangle + \langle a_1a_1 \| a_3a_1\rangle \\ & + \langle a_1a_4 \| a_3a_4\rangle - (\langle a_1a_1 \| a_1a_1\rangle \\ & + \langle a_1a_3 \| a_1a_3\rangle + \langle a_1a_4 \| a_1a_4\rangle) S_\sigma',\end{aligned} \tag{A2}$$

$$\mathcal{H}_{134}{}^{AC} = \langle a_4a_1 \| a_1a_4\rangle S_\sigma', \tag{A3}$$

$$\mathcal{H}_{34}{}^{CC} = \langle a_4a_1 \| a_1a_4\rangle, \tag{A4}$$

$$\mathcal{H}_{34}{}^{AA} = \langle a_3a_4 \| a_4a_3\rangle, \tag{A5}$$

$$\mathcal{H}_{134}{}^{AA} = \langle a_4a_1 \| a_3a_4\rangle S_\sigma', \tag{A6}$$

$$\mathcal{H}_{13,24}{}^{AC} = \langle a_4a_1 \| a_3a_4\rangle, \tag{A7}$$

$$\begin{aligned}\mathcal{H}_I{}^{AB} - \mathcal{H}_I{}^{AA}S_\sigma = {} & \langle a_1 | \mathcal{H}_1 | b_1\rangle - \langle a_1 | \mathcal{H}_1 | a_1\rangle S_\sigma \\ & + \langle a_1a_1 \| b_1a_1\rangle + \langle a_1a_3 \| b_1a_3\rangle \\ & + \langle a_1a_4 \| b_1a_4\rangle - (\langle a_1a_1 \| a_1a_1\rangle \\ & + \langle a_1a_3 \| a_1a_3\rangle + \langle a_1a_4 \| a_1a_4\rangle) S_\sigma,\end{aligned} \tag{A8}$$

$$\mathcal{H}_{14,23}{}^{AB} = \langle a_4a_1 \| b_1a_4\rangle S_\sigma'^2, \tag{A9}$$

$$\mathcal{H}_{134}{}^{BC} = \langle a_4b_1 \| a_1a_4\rangle S_\sigma', \tag{A10}$$

$$\mathcal{H}_{14,23}{}^{BB} = \langle a_4a_1 \| b_1a_4\rangle S_\sigma'^2. \tag{A11}$$

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[19] G. Blasse, J. Phys. Chem. Solids **26**, 1969 (1965).