PHONON-INDUCED SUPEREXCHANGE

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Received 2 September 1975

The superexchange in $V^{2+} - O^{2-} - V^{2+}$ pair in MgO is calculated including the orbit-lattice interaction into the one-electron hamiltonian. Although the exchange by itself is ferromagnetic, the phonon-induced contribution is found to be dominantly antiferromagnetic.

We wish to present a new superexchange mechanism which arises as a result of contributions of the spin-phonon interaction to the energy of singlet and triplet states in a four-electron three-center model.

We consider the configurations (A) $V^{2+} - O^{2-} - V^{2+}$, (B) $V^{+} - O^{-} - V^{2+}/V^{2+} - O^{-} - V^{+}$ and (C) $V^{+} - O^{2-} - V^{3+}/V^{3+} - O^{2-} - V^{+}$. The excitations to (B) and (C) arise from (A) as a result of virtual absorption or emission of phonons through the orbit-lattice interaction,

$$H' = \sum_{j=1}^{21} V_j Q_j$$

where the V_j are the spatial derivatives of the crystal potential and Q_j are the collective coordinates [1–3]. The calculation of the superexchange for the static hamiltonian,

$$H_0 = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{ig} \frac{z_g e^2}{r_{ig}} + \sum_{ij}{}' \frac{e^2}{r_{ij}}$$

has been performed by Huang [4] and we shall trust her computation and the unperturbed values of energy differences of the configurations (A), (B) and (C), which are not too easily predicted. Following the standard procedure, we calculate the energy of the singlet state W_s and that of the triplet state W_t form the hamiltonian $H = H_0 + H'$. The exchange in the equivalent hamiltonian $-2J_{34} s_3 \cdot s_4$ is then defined by $2J_{34} = W_s - W_t$. Assuming, a_1 and a_2 electron orbitals as p_z on the central atom and $a_3 = d_{xz}$, $a_4 = d_{xz}$, $b_1 = d_{z^2}$ on the magnetic atom, the result of calculations for the phonon-induced exchange is,

$$J_{34} = J_A^{(1)} + J_B^{(2)} + J_C^{(2)} + J_B^{(3)} + J_C^{(3)}$$

where

$$J_A^{(1)} = 2\langle a_3|H'|a_4\rangle T - 2\langle a_3|H'|a_3\rangle T^2 - 2\langle a_1|H'|a_4\rangle S_\pi T$$

$$\begin{aligned} J_B^{(2)} = {} & -8\,\Delta_B^{-1}(\langle a_1|H'|b_1\rangle - \langle a_1|H'|a_1\rangle S_\sigma)\,[\langle a_1|H'|b_1\rangle T^2 + 2\langle a_3|H'|a_4\rangle S_\sigma T \\ & - (\langle a_1|H'|a_1\rangle + 2\,\langle a_3|H'|a_3\rangle)\,S_\sigma T^2 - \tfrac{1}{2}\langle a_4|H'|b_1\rangle S_\pi T] \end{aligned}$$

$$\begin{aligned} J_C^{(2)} = {} & 4\,\Delta_C^{-1}(\langle a_1|H'|a_3\rangle - \langle a_1|H'|a_1\rangle S_\pi)\,[\langle a_1|H'|a_4\rangle T + \langle a_1|H'|a_4\rangle S_\pi^2 T \\ & - \{2\langle a_4|H'|a_3\rangle S_\pi T + \langle a_1|H'|a_3\rangle T^2 - (\langle a_1|H'|a_1\rangle + 2\,\langle a_3|H'|a_3\rangle) S_\pi T^2\}] \end{aligned}$$

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$$J_B^{(3)} = 4\Delta_B^{-2}\,(\langle a_1|H'|b_1\rangle - \langle a_1|H'|a_1\rangle S_\sigma)^2\,[(H_{34}^{BB} - H_I^{AA}T^2) + \tfrac{1}{2}H_{1423}^{BB}]$$
$$+\ 4\Delta_B^{-2}(\langle a_1|H'|b_1\rangle - \langle a_1|H'|a_1\rangle S_\sigma)\,[\langle b_1|H'|b_1\rangle T^2 + 2\langle a_3|H'|a_4\rangle T$$
$$-\ (\langle a_1|H'|a_1\rangle + 2\langle a_3|H'|a_3\rangle)T^2]\,[H_I^{AB} - H_I^{AA}S_\sigma]$$
$$J_C^{(3)} = 2\Delta_C^{-2}\,(\langle a_1|H'|a_3\rangle - \langle a_1|H'|a_1\rangle S_\pi)^2 H_{34}^{CC}$$
$$+\ 2\Delta_C^{-2}\,(\langle a_1|H'|a_3\rangle - \langle a_1|H'|a_1\rangle S_\pi)\langle a_1|H'|a_4\rangle S_\pi^2\,T\,(H_{13}^{AC} - H_I^{AA}S_\pi),$$

with

$S_\pi = \langle p_z|d_{xz}\rangle$, $S_\sigma = \langle p_z|d_{z^2}\rangle$, $T = \langle d_{xz}|d_{xz}\rangle$.

H_I^{AA} is the unperturbed energy of the configuration (A), $\Delta_B = H_I^{BB} - H_I^{AA}$, $\Delta_C = H_I^{CC} - H_I^{AA}$, in the notation of ref. [4]. In the harmonic approximation, $J_A^{(1)} = 0$. Further in view of the symmetry rules, the dominant terms are,

$$J_B^{(2)} = 8\Delta_B^{-1}\langle a_1|H'|a_1\rangle S_\sigma\,[2\langle a_3|H'|a_4\rangle S_\sigma T - S_\sigma T^2(\langle a_1|H'|a_1\rangle + 2\langle a_3|H'|a_3\rangle)]$$
$$J_C^{(2)} = 4\Delta_C^{-1}\langle a_1|H'|a_1\rangle S_\pi\,[2\langle a_4|H'|a_3\rangle S_\pi T - (\langle a_1|H'|a_1\rangle + 2\langle a_3|H'|a_3\rangle)S_\pi T^2]$$
$$J_B^{(3)} = 4\Delta_B^{-2}(\langle a_1|H'|a_1\rangle S_\sigma)^2\,[H_{34}^{BB} - H_I^{AA}T^2] + 4\Delta_B^{-2}(-\langle a_1|H'|a_1\rangle S_\sigma)\,[\langle b_1|H'|b_1\rangle T^2 + 2\langle a_3|H'|a_4\rangle T$$
$$-\ (\langle a_1|H'|a_1\rangle + 2\langle a_3|H'|a_3\rangle)T^2]\,[H_I^{AB} - H_I^{AA}S_\sigma].$$

Since the collective coordinates are mutually orthogonal, we can ignore the cross terms, so that,

$$J_B^{(2)} = -8\Delta_B^{-1}\langle a_1|H'|a_1\rangle^2 S_\sigma^2 T^2, \qquad J_C^{(2)} = -4\Delta_C^{-1}\langle a_1|H'|a_1\rangle^2 S_\pi^2 T^2,$$
$$J_B^{(3)} = 4\Delta_B^{-2}\,(\langle a_1|H'|a_1\rangle S_\sigma)^2\,[H_{34}^{BB} - H_I^{AA}T^2], \qquad J_C^{(3)} = 2\Delta_C^{-2}\,(\langle a_1|H'|a_1\rangle S_\pi)^2 H_{34}^{CC}$$

in which the first three terms are antiferromagnetic while the last term $J_C^{(3)}$ is ferromagnetic. Since $H_{34}^{CC} = 0.0036$, $H_{34}^{BB} - H^{AA}T^2 = -0.0059$, $\Delta_B = 0.59$, $\Delta_C = 0.69$, $S_\pi = 0.082$, $S_\sigma = -0.104$, $T = 0.023$ a.u. for $R = 2.1$ A, with the orbit-lattice interaction corresponding to p electrons,

$$J_{phn} = -6\,\langle a_1|\Sigma_{j=7}^{12}\,V_j|a_1\rangle^2\,\epsilon^2 \times 10^{-4}\ \text{a.u.}$$

where the isotropic odd strain is

$$\epsilon^2 = \frac{3\hbar R^2}{4\rho\pi^2}\,(\tfrac{2}{3}v_\ell^{-7} + v_t^{-7})\left(\frac{k}{\hbar}\right)^6 T^6 \int_0^{\theta/T}\left(\frac{1}{e^x - 1} + \frac{1}{2}\right)x^5\,dx$$

with R the lattice constant, ρ the mass density, v_t and v_ℓ the transverse and longitudinal sound velocities and θ is the Debye cutoff. Upon substituting the values [5] as appropriate to MgO, and our estimated value $\langle a_1|\Sigma\,V_j|a_1\rangle = 1.0$ a.u., we find that the zero-point contribution to the exchange is

$$J_{phn}(0) = -71 \times 10^{-6}\ \text{a.u.} = -25\ \text{K}.$$

This antiferromagnetic value is 15% of Huang's calculated static antiferromagnetic contribution of −165 K and 10% of ferromagnetic value of +256 K. Apart from the zero-point phonon contribution, the temperature dependent part is

$$J_{phn}(T) = -6.7 \times 10^{-21}\,T^6 \int_0^{\theta/T}(\exp x - 1)^{-1}\,x^5 dx\ \text{a.u.}$$

which is antiferromagnetic whereas the static total rigid-lattice value is ferromagnetic. Therefore, at some tempera-

ture the exchange can go to zero and a line width divergence at high temperatures is possible. If however the exchange and the phonon-induced exchange have the same sign, apparently a large exchange is possible and may be noted in terms of line narrowing at high temperatures in paramagnetic crystals. In general, both the ferro- as well as the antiferromagnetic pairing of spins is possible through our mechanism since the energy contributions to both the singlet and triplet states are predicted.

References

[1] J.H. Van Vleck, Phys. Rev. 57 (1940) 426.
[2] S. Koide and M.H.L. Pryce, Phil. Mag. 3 (1958) 607.
[3] K.N. Shrivastava, Phys. Reports (1975).
[4] N.L. Huang, Phys. Rev. 157 (1967) 378.
[5] K.N. Shrivastava, Phys. Rev. 187 (1969) 446.