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BIQUADRATIC SUPEREXCHANGE*

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Recently, Harris and Owen[1,2] found it necessary to invoke a biquadratic exchange interaction in order to explain the energy level spectrum of Mn pairs in MgO. They used the expression

$$\mathcal{H} = J(\vec{S}^a \cdot \vec{S}^b) - j(\vec{S}^a \cdot \vec{S}^b)^2 \qquad (1)$$

to fit the nearest-neighbor pair spectrum with $J/k = 14.6°\mathrm{K}$, $j/k = 0.73°\mathrm{K}$, and $j/J = 0.05 \pm 0.03$. We have investigated the origin of the biquadratic exchange integral (j) and we have derived an explicit expression for j using a technique first employed by Keffer and Oguchi[3] to find the ordinary bilinear exchange integral (J). Anderson[4] first pointed out the possibility of a biquadratic superexchange interaction and roughly estimated its magnitude. Until now, however, there existed no quantitative treatment which could show that, in fact, a superexchange interaction was large enough to be responsible for the magnitude of j. This is necessary because an effective biquadratic exchange term can also arise via a mechanism[5] in which a balance is set up between elastic and exchange forces. Such a contribution to j is difficult to estimate, but Harris and Owen[1] state that it is too small to explain the observed value.

We have utilized the method of Keffer and Oguchi[3] to investigate terms in the superexchange problem quadratic in $\vec{S}^a \cdot \vec{S}^b$. Their procedure follows the treatment of permutation degeneracy due to Serber[6] (see also Anderson[7]) and treats the following three configurations:

Configuration A,
$\mathrm{Mn}^{++}(3) - \mathrm{O}^{--}(1,2) - \mathrm{Mn}^{++}(4)$;

Configuration B,
$\mathrm{Mn}^{++}(3) - \mathrm{O}^{-}(4) - \mathrm{Mn}^{+}(1,2)$;

Configuration C,
$\mathrm{Mn}^{+}(1,2) - \mathrm{O}^{-}(3) - \mathrm{Mn}^{++}(4)$;

where the numbers in parentheses label the electron orbitals. Configuration A is referred to as ionic. If the overlap integral between the Mn^{++} $3d$ electrons and the O^{--} $2p$ electrons[8] is designated by S, Keffer and Oguchi show that J is of order S^4, a result first pointed out by Yamashita and Kondo.[9] In particular, they find

$$J = -2S^4\{q_{13,24}{}^{AA} + 2[(q_{14}{}^{BA})^2(q_{34}{}^{BB} + q_{13,24}{}^{CB})/(q_1{}^{BB})^2] - 4(q_{14}{}^{BA}q_{134}{}^{BA}/q_1{}^{BB})\}, \qquad (2)$$

where $q_1{}^{BB}$ is a measure of the transfer energy; that is, the energy difference between the ground (ionic) configuration A and the excited configuration B. The other terms represent the matrix elements of the Hamiltonian between different orbitals (i.e., $q_{13,24}{}^{CB}$ is related to the matrix element of the Hamiltonian between configurations C and B with orbitals 1 and 3 in configuration C, and 2 and 4 in configuration B, permuted respectively).

We have extended the treatment of Keffer and Oguchi to powers of S higher than fourth. We find the ionic contribution alone does give rise to a biquadratic exchange term, but one proportional to S^8. Using the approximate value $S \simeq 0.05$, this implies $j/J = S^4 = 10^{-5}$, a result much too small. Upon consideration of the excited configurations B and C, however, we find that a biquadratic term appears first in terms of order S^6. This is in striking contrast to the result for the ordinary exchange integral in which the ionic and excited configurations contribute about equally to J, both being proportional to S^4. In detail, we find

$$j = \frac{8S^6}{q_1{}^{BB}}\left[q_{134}{}^{BA} - \frac{q_{14}{}^{BA}}{q_1{}^{BB}}(q_{34}{}^{BB} + q_{13,24}{}^{CB})\right]^2. \qquad (3)$$

There appears to be no simple relation between j and J, but it is interesting that j must be positive because of the square in (3). It is clear that in the limit of large transfer energies $(q_1^{BB} \to \infty)$ the S^6 contribution to j will vanish, an expression of our earlier result that the ionic term contributes first to j terms of order S^8.

Anderson estimated that $j \sim b^4/U^3$ where b was a transfer integral and U a transfer energy. Our result is in agreement with his if we make the reduction associated with the neglect of terms in the Hamiltonian containing S explicitly. We find $j = 8b^2(J' + J'')^2/(\Delta E)^3$ where J' and J'' are the Anderson and Anderson-Hasegawa exchange integrals, respectively, ΔE is the energy difference between excited and ground configurations, and b, with the neglect of some Coulombic terms, is Anderson's transfer integral.

We have used Keffer and Oguchi's values appropriate to MnO for the various overlap integrals appearing in (3) and have estimated the transfer energy q_1^{BB} in a manner similar to Kondo.[10] We find $q_1^{BB} \sim 14$ eV and, using this value, find the results shown in the following table:

	J(°K)	j(°K)	j/J
Calc. (MnO)	43.5	0.70	0.016
Exp. (MnO, reference 2)	11		0.01 - 0.02
Calc. (Mn^{++} in MgO)	60.9	1.37	0.022
Exp. (Mn^{++} in MgO, reference 1)	14.6	0.73	0.05 ± 0.03

The theoretical results for MnO are in reasonable agreement with the results of Rodbell et al.[2] considering the approximate nature of the overlap integral computation. In particular, we expect the ratio of j/J to be rather more accurate than either our result for j or J alone. Indeed, it is seen that our value of j/J lies within the experimental range of error. Our MnO results are not in very close agreement with the pair spectrum values, but this is to be expected because of the difference in lattice constant between MnO and MgO. We have applied Harris and Owen's empirical factor of 1.4 for J and $(1.4)^2$ for j in arriving at the results presented in the third line of the above table.

We are in the process of computing the overlap integrals more carefully for Mn^{++} ions in both MnO and MgO using Hartree-Fock wave functions. We hope this will improve the accuracy of our results and will warrant similar calculations for other salts. In any case, we have certainly shown here that the usual superexchange mechanism is fully capable of explaining the origin and magnitude of the biquadratic exchange interaction.

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EFFECT OF PREFERRED ORIENTATION ON THE ELECTRICAL RESISTIVITY OF ALPHA PLUTONIUM AT LOW TEMPERATURES*

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The electrical resistivity of monoclinic alpha-phase plutonium is known to rise rapidly between 4°K and 105°K, and then to decrease slowly to 388°K (at the $\alpha \to \beta$ transition). We have now found this behavior to be strongly affected by preferred orientation of the polycrystalline grain structure.

Oriented specimens were prepared by heating plutonium to a temperature high in the beta-phase region, where a compressive load of 60 000 psi