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Mn^{2+}-F-Fe^{2+} Exchange Interactions

G. K. WERTHEIM AND H. J. GUGGENHEIM
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

AND

M. BUTLER* AND V. JACCARINO*
Department of Physics, University of California, Santa Barbara, California 93106

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The Néel temperature in $Mn_{1-x}Fe_xF_2$ has a parabolic dependence on concentration with a maximum near $x=0.75$, indicating that the effective exchange energy for unlike ions is significantly greater than the geometric mean of those for manganese and iron. Comparison with NMR results suggests that this is due to an enhanced near-neighbor ferromagnetic exchange between unlike ions.

IN a recent study of the critical-point behavior of Fe^{2+} in MnF_2, it was noted that the Néel temperature T_N of MnF_2 is modified more by the presence of FeF_2 than is predicted by a linear interpolation based on concentration.[1] A linear behavior was reported some years ago in mixed cobalt and manganese oxides.[2] It was, there, shown using molecular field theory that such a behavior is predicted only if the unlike-ion exchange has a particular value, namely, the geometric mean of the like-ion exchange interactions. This is plausible in the context of superexchange theory for the case of the Anderson exchange mechanism. However, it was subsequently found by Hashimoto[3] that the Néel temperatures in mixed perovskite fluorides are not linear functions of concentration. Such small deviations from linearity may be indicative of the limited validity of molecular field theory or that mechanisms other than that of Anderson may be important.

Although molecular field theory is quite inaccurate at predicting T_N, it is relatively successful at predicting quantities which depend on *changes* in the effective field and not its absolute value, e.g., the susceptibility. Thus one might expect molecular field theory to be more appropriate for predicting the concentration dependence of T_N in mixed crystals than T_N for the pure crystals. If we consider the case of a two-sublattice antiferromagnet occupied randomly by two magnetic ions (denoted by subscripts a and b), molecular field theory yields

$$T_N=\tfrac{1}{2}[\sigma T_a+(1-\sigma)T_b]+\{\tfrac{1}{4}[\sigma T_a+(1-\sigma)T_b]^2+\sigma(1-\sigma)(T_{ab}^2-T_aT_b)\}^{1/2}, \quad (1)$$

where σ is the concentration of a ions, $T_a=2S_a(S_a+1)\times|z_1J_1^a-z_2J_2^a|/3k$ is the Néel temperature of a lattice of a ions, T_b that of b ions, and

$$T_{ab}\equiv 2[S_a(S_a+1)S_b(S_b+1)]^{1/2}|z_1J_1^{ab}-z_2J_2^{ab}|/3k.$$

Subscripts 1 and 2 refer to interactions between ions on the same and opposite sublattices, respectively. Likewise, the susceptibility of such a system is

$$\chi=\frac{\sigma C_a+(1-\sigma)C_b+\sigma(1-\sigma)DT^{-1}}{T+[\sigma\theta_a+(1-\sigma)\theta_b]+\sigma(1-\sigma)ET^{-1}}, \quad (2)$$

where C_a is the Curie constant of a lattice of a ions, C_b that of b ions; θ_a is the paramagnetic Curie point of a lattice of a ions, θ_b that of b ions;

$$E=\theta_a\theta_b-\theta_{ab}^2;\quad D=\theta_aC_a+\theta_bC_b-2\theta_{ab}(C_aC_b)^{1/2};$$

and

$$\theta_{ab}\equiv 2[S_a(S_a+1)S_b(S_b+1)]^{1/2}|z_1J_1^{ab}+z_2J_2^{ab}|/3k.$$

(Notice the similarity to the susceptibility derived for ferrimagnets.)

In the perovskites, the exchange is dominantly with the six nearest-neighbor (nn) magnetic ions on the opposite sublattice,[4,5] i.e., $z=6$, and only one exchange constant is needed. In the rutile structure, the two nearest neighbors are on the same sublattice and have weak ferromagnetic coupling while the eight next-nearest neighbors (nnn) on the opposite sublattice have antiferromagnetic exchange. It is apparent from Eq. (1) that, within the confines of molecular field theory, these two exchange interactions appear additively in the definition of T_a, T_b, and T_{ab}, and, therefore, cannot be separated experimentally on the basis of T_N alone. However, measurements of T_{ab} and θ_{ab} would permit both J_1^{ab} and J_2^{ab} to be determined. The special case $T_{ab}^2=T_aT_b$ corresponds to the linear behavior of Ref. 2. As an index of the deviation from this case we define

$$R_{ab}=2\frac{[J_{ab}-(J_aJ_b)^{1/2}]}{|J_a-J_b|},$$

where $J_\alpha\equiv(z_2J_2^\alpha-z_1J_1^\alpha)$ with $\alpha=a$, b, or ab. Thus, for the special case where J_{ab} is the geometric mean of J_a and J_b, $R_{ab}=0$.

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[1] G. K. Wertheim, H. J. Guggenheim, and D. N. E. Buchanan, Phys. Rev. Letters **20**, 1158 (1968).

[2] G. E. Bacon, R. Street, and R. H. Tredgold, Proc. Roy. Soc. **217**, 252 (1953).

[3] T. Hashimoto, J. Phys. Soc. Japan **18**, 1140 (1963).

[4] C. G. Windsor and R. W. H. Stevenson, Proc. Phys. Soc. (London) **87**, 501 (1966).

[5] J. S. Pickart, M. F. Collins, and C. G. Windsor, J. Appl. Phys. **37**, 1054 (1966).

EXPERIMENTAL

We have examined the concentration dependence of T_N in the rutile structure system $Mn_{1-x}Fe_xF_2$, using the ^{57}Fe Mössbauer effect (ME). Samples were prepared by melting together weighed amounts of MnF_2 and FeF_2 in an argon atmosphere. Differential thermal analysis showed solid solubility over the entire range of composition. ME absorbers were prepared from crushed powders incorporated into a plastic binder. The actual composition of the materials used was obtained by wet-chemical analysis. The perovskite $RbMn_{0.5}Fe_{0.5}F_3$ was examined as a loosely packed powder. Data were taken either with the sample immersed in liquid nitrogen, in which case the temperature was controlled via the vapor pressure, using a Cartesian diver manostat, or with the sample on a heater-and-thermocouple-controlled cold finger in the Dewar vacuum. The ME studies utilized a conventional constant-acceleration doppler effect spectrometer with a ^{57}Co-in-palladium source.

T_N was determined by two independent techniques. Data below T_N were analyzed to obtain the effective magnetic field H at the iron nucleus. The ordering temperature was obtained as the intercept of a linear extrapolation to $H^3=0$ on a H^3 versus T plot. Data above T_N were analyzed to obtain the fraction of the absorption remaining in the paramagnetic, quadrupolar doublet. T_N was defined by the vanishing of the paramagnetic absorption. A temperature range of about 3°K was covered in each case in order to locate T_N to ± 0.1°K.

RESULTS AND DISCUSSION

The ME results on $Mn_{1-x}Fe_xF_2$ are summarized in Fig. 1. They are well represented by the parabolic behavior of Eq. (1) with $T_{ab}=83.4$°K, which corresponds to $R_{MnFe}=+0.57$. In $RbMn_{1-x}Fe_xF_3$, we obtain $R_{MnFe}=-0.28$. The T_N of $RbMnF_3$ was taken as 83.0°K[6] and that of $RbFeF_3$ as 102°K.[7]

The result in the mixed Mn-Fe perovskite, where the exchange is predominantly with the nn ions, shows that in the context of molecular field theory the exchange between Fe^{2+} and Mn^{2+} is not necessarily equal to the geometric mean of the like-ion exchanges. This is in accord with the work of Hashimoto[3] in other mixed perovskite fluorides. Using his data for $KMn_{1-x}Ni_xF_3$ and $KMn_{1-x}Co_xF_3$, we obtain $R_{MnNi}=-0.15$ and $R_{MnCo}=+0.21$ from the variation of T_N with concentration. The small deviation of R from zero in the three perovskites may result from a change in the antiferromagnetic exchange between the sublattices or from implicit limitations of the molecular field description of T_N. This could be settled by meaningful paramagnetic Curie-point measurements.

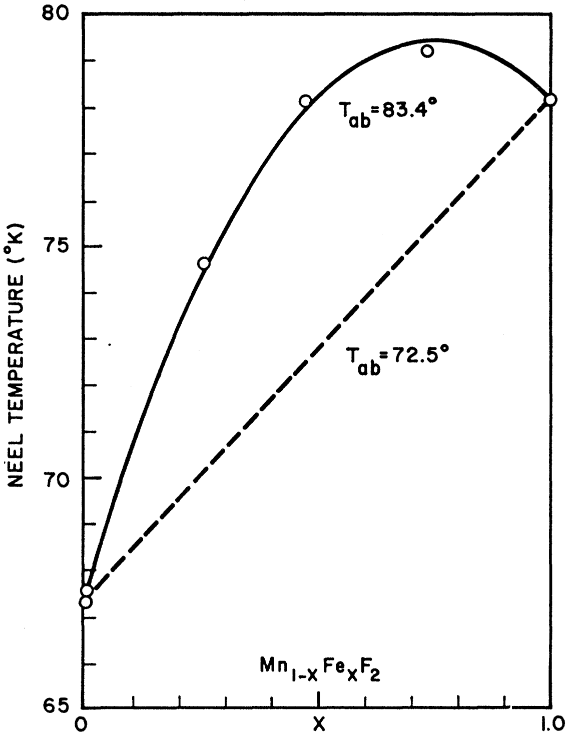

FIG. 1. Néel temperature in the system $Mn_{1-x}Fe_xF_2$. The point for pure MnF_2 is taken from P. Heller, Phys. Rev. **146**, 403 (1966), that for FeF_2 and $Mn_{0.993}Fe_{0.007}F_2$ from Ref. 1.

In the *pure* rutile-structure fluorides the *nn* ferromagnetic exchange within a sublattice is usually weak compared to the *nnn* exchange between ions on different sublattices.[8] Thus the relatively large R_{MnFe} (it is twice as great as that in any other case) could be due either to increased *nn* ferromagnetic exchange or increased *nnn* antiferromagnetic exchange. Néel temperature measurements cannot distinguish between these two alternatives. However, ^{19}F NMR studies in MnF_2 below T_N with Fe^{2+} impurities[9] indicate strong ferromagnetic exchange between *nn* impurity and host ions. In the light of the NMR results the increased effective unlike-ion exchange obtained from the T_N may be attributed largely to the *nn* ferromagnetic coupling. The relatively weak Mn-F-Fe antiferromagnetic coupling in $RbMn_{1-x}Fe_xF_3$ supports this interpretation although it is not known to what extent this result obtained in a perovskite would apply in the rutile structure. Further work is in progress to obtain meaningful paramagnetic Curie-point data.

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[6] D. T. Teaney, V. L. Moruzzi, and B. E. Argyle, J. Appl. Phys. **37**, 1122 (1966).

[7] G. K. Wertheim, H. J. Guggenheim, H. J. Williams, and D. N. E. Buchanan, Phys. Rev. **158**, 446 (1967).

[8] G. G. Low, A. Okazaki, R. W. H. Stevenson, and K. C. Turberfield, J. Appl. Phys. **35**, 998 (1964).

[9] M. Butler, N. Kaplan, V. Jaccarino, and H. J. Guggenheim (unpublished).