

which stoichiometry is notoriously difficult to achieve. The stability of Fe^{+3} as an impurity in these materials is perhaps not too surprising. Experiments interpreted in terms of metastable multiple-charge states have been reported on several other materials which, in addition to not being oxides, are good insulators and in which, therefore, metastable charge states may be expected to remain stable for long periods.³⁻⁷ Measurements on a number of such systems are in progress utilizing shorter lived nuclear levels as well as Fe^{57} .

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¹⁵Bhide and Shenoy⁹ find the ferrous linewidth to be greater than the ferric linewidth, and to decrease with increasing temperature. Our measurements show that above the Néel temperature the ferrous line is somewhat broadened, but that the width is essentially temperature independent. The data of Bhide and Shenoy at room temperature and above are consistent with an almost temperature-independent linewidth of about 1.3 times the natural width. The broadening of the ferric line indicates an inhomogeneous local environment, which is consistent with the cation stabilization model.

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ZERO-POINT SPIN DEVIATION IN ANTIFERROMAGNETS

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Spin-wave theories of antiferromagnets predict a zero-point spin deviation of a few percent from the completely ordered state. Attempts have been made to observe this effect by using nmr measurements in the antiferromagnetic state to find the effective field acting on the nuclei of the magnetic ions. The largest part of this field is $A\langle S \rangle$ where $A\vec{S} \cdot \vec{I}$ is the hyperfine interaction and $\langle S \rangle$ is the time-averaged electronic spin. The value of A is usually taken from esr data on magnetically dilute salts and hence $\langle S \rangle$ can be deduced. This procedure has been followed in some recent investigations

of Mn^{2+} antiferromagnets with the results given in Table I. The predicted deviations are not observed; the experimental values are consistently higher than expected. The observation of $\langle S \rangle / S > 1$ is clearly anomalous and several authors¹⁻³ have suggested that the assumed value of A may be in error. In this Letter we propose that $A(\text{Mn}^{2+})$ is in fact larger in the antiferromagnetic state due to the transfer of unpaired electron spin from one magnetic ion to the next.

There is experimental evidence that such transfers can be appreciable. For example,

Table I. Time-averaged electron spin for several Mn^{2+} antiferromagnets.

Antiferromagnet	$\langle S \rangle / S$		Reference
	Theory	Experiment	
MnF ₂	97.6 %	99.6 %	a
KMnF ₃	97.0	98.4	b
CsMnF ₃	95.6	97.0	c
MnO	97.0	102.4	d
α -MnS	96.8	103.3	e

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we find from ENDOR measurements⁴ on the structure $Fe^{3+}-O^{2-}-Al^{3+}$ in the salt $Fe:LaAlO_3$ that there is a transferred hyperfine interaction, $a\vec{S}_1 \cdot \vec{I}_1$, between the Fe^{3+} ion ($S = \frac{5}{2}$) and the ^{27}Al nucleus ($I = \frac{5}{2}$) with $a = +1.1 \times 10^{-4} \text{ cm}^{-1}$. There are also smaller anisotropic terms. (For other examples, see Laurance, McIrvine, and Lambe,⁵ Chen, Kikuchi, and Watanabe,⁶ and Hubbard, Rimmer, and Hopgood.⁷ We attribute a large part of this interaction to unpairing of the spins in the $2s$ orbit on the Al^{3+} ion (configuration $1s^2 2s^2 2p^6$) by the unpaired d electrons on Fe^{3+} via overlap with a σ bonding orbit on the O^{2-} ligand. In the case of two neighboring Mn^{2+} ions (configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$), a similar unpairing of the spins in a $3s$ orbit might be expected to give rise to a transferred hyperfine interaction of comparable magnitude.

The mechanism can be illustrated by the following example. Consider the 180° structure $Mn_1^{2+}-F^- - Mn_2^{2+}$ which is a nearest-neighbor pair in $KMnF_3$. The $2p_\sigma$ orbit on F^- is known⁸ to contain a fraction f_σ of unpaired spin which has been transferred from a d orbit on Mn_2 . This can be partly transmitted to a $3s$ orbit on Mn_1 by the overlap $S_\sigma = \langle 3s | 2p_\sigma \rangle$ giving an unpaired spin density $f_\sigma S_\sigma^2$ in the $3s$ orbit. The hyperfine interaction for Mn_1 is then

$$A\vec{S}_1 \cdot \vec{I}_1 + a\vec{S}_2 \cdot \vec{I}_1, \quad (1)$$

where $S_1 = S_2 = \frac{5}{2}$, $I = \frac{5}{2}$ for ^{55}Mn , $A = -91 \times 10^{-4} \text{ cm}^{-1}$ for an isolated Mn^{2+} ion in $KMgF_3$,⁹ and

$$a = f_\sigma S_\sigma^2 A_{3s}, \quad (2)$$

where A_{3s} is the hyperfine interaction corresponding to a $3s$ orbit being singly occupied. Using the values $A_{3s} = 0.43 \text{ cm}^{-1}$,¹⁰ $f_\sigma \approx 1.2\%$,¹¹ and assuming $\langle 3s | 2p_\sigma \rangle \approx \langle 3d_\sigma | 2p_\sigma \rangle = 0.09$,⁷ we then find $a \approx +0.42 \times 10^{-4} \text{ cm}^{-1}$. This estimate should not be taken too seriously since other transfer processes can also contribute, but we believe that the sign and order of magnitude are correct.

In an nmr experiment the field at the nucleus will now be

$$A'\langle S \rangle = A\langle S_1 \rangle + \sum_i a_i \langle S_i \rangle, \quad (3)$$

where the sum can probably be limited to those neighbors connected to S_1 by paths which include only one ligand. For $KMnF_3$ there are six such neighbors, all antiparallel to S_1 below the Néel temperature, so we expect A' (antiferro) $= A - 6a$. If $A = -91 \times 10^{-4} \text{ cm}^{-1}$ ¹² and $a = +0.42 \times 10^{-4} \text{ cm}^{-1}$, then $A' = -93.5 \times 10^{-4} \text{ cm}^{-1}$. This is an increase of 2.8% which compares with the increase of 1.4 to 2% which is required to account for the fluoride results in Table I. For antiferromagnetic MnO the only neighbors which will contribute to the present effect are the six antiparallel ones joined to S_1 by 180° paths, so the argument is the same. However, the covalency and overlap are expected to be stronger for the oxide so a larger increase in hyperfine structure is expected. Similarly, for the sulfide the effect should be even larger and this trend is observed in Table I.

Our estimated value for a in $KMnF_3$ is very approximate. The $2s$ orbit on the ligand will also contribute and because of the relative signs of the overlaps involved it will reduce this value. Also, the small overlaps with the $1s$ and $2s$ orbits on Mn^{2+} may be important. Furthermore, transfer into $4s$ and $3d$ orbits will contribute, but we estimate that these effects are relatively small. In the case of 90° path through a ligand, such as occurs for nearest neighbors in MnO , direct overlap between a d orbit on one Mn^{2+} and a $3s$ orbit on the other will tend to cancel the effect produced by the path through the ligands. It is also by no means certain that A (isolated) is exactly the same in a dilute salt as in a concentrated salt since, among other things, there may be small changes in ligand-metal-ion distance. In view of these various effects an exact numerical comparison between theory and experiment is likely to be quite difficult.

Finally, it may be noted that the present mod-

el predicts a decrease in effective hyperfine structure in the paramagnetic state. Using Eq. (3) on KMnF_3 , for example, we predict $A'(\text{para})=A+6a$ compared with $A'(\text{isolated})=A$ and $A'(\text{antiferro})=A-6a$. There is some indication that such an effect occurs in $\alpha\text{-MnS}$ ¹³ and in MnSe ¹⁴ though it does not appear to be present in MnO .¹⁵ Further experimental data on this point are very desirable.

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MICROWAVE-ENHANCED CRITICAL SUPERCURRENTS IN CONSTRICTED TIN FILMS

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We have found that the value of the maximum supercurrent, at zero voltage, that can flow through a constriction in a tin film depends on both the temperature and the incident microwave power at the constriction, and that under certain conditions the critical current is larger than its value without microwaves at the same temperature.

The effect of microwaves on a constricted thin film superconductor was first investigated by Anderson and Dayem.¹ They found that at certain microwave powers and at certain non-zero voltages the current through the constriction could be increased without any change in voltage. The voltages (V) at which this could occur were found to be simply related to the frequencies (ν) of the microwaves by $2eV = nh\nu$, where n is an integer. This behavior is very similar to that of a Josephson junction² which was measured by Shapiro.³ However, Anderson and Dayem found instability at low voltages and so did not find the zero-voltage effect which we have observed.

In our experiment the tin, which was approximately 2000 Å thick, was evaporated through a mask on to a glass substrate, giving the same geometry to that used by Anderson and Dayem. The widths of the constrictions were between 3 and 4 μ . Many samples were made under identical conditions and they all behaved similarly. The sample was placed in a wave guide which had a stationary wave inside it. The position of the sample was such that the transport current in it was parallel to, and coincident with, the maximum electric field of the microwaves. The film extended beyond the walls of the wave guide so that current and voltage leads could be attached to it. The sample was screened from magnetic fields with an iron cylinder.

Because the wave guide and the specimen were immersed in liquid helium the temperature of the film was always the same as the bath, and during measurements the pressure was kept constant to within an equivalent temperature of $\pm 10^{-4} \text{ K}$, although the absolute ac-