EXCHANGE SPLITTING OF THE GROUND STATE OF Ni²⁺ IONS IN ANTIFERROMAGNETIC MnF₂, KMnF₃, AND RbMnF₃

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(Received 4 May 1966)

In earlier papers fluorescence from divalent nickel ions in the nonmagnetic crystals MgF_2, ZnF_2, and $KMgF_3$ was reported.[1,2] The fluorescence consists of a group of strong and narrow zero-phonon lines, representing magnetic dipole transitions between the $^3T_2$ first excited state and the $^3A_2$ ground state of the Ni²⁺ ion, accompanied by a broad vibronic sideband. Optical measurements have now been extended to Ni²⁺ ions in the antiferromagnetic hosts MnF_2, $KMnF_3$, and $RbMnF_3$. The principal results can be stated briefly as follows[3]: (1) At low temperature the ground state, $^3A_2$, of Ni²⁺ is observed to be split by the exchange field of the magnetically ordered host. (2) The splittings of some of the sidebands agree with the zone-boundary magnon frequencies determined by neutron scattering. (3) Very efficient energy transfer from the host Mn²⁺ ions to Ni²⁺ ions is observed.

Evidence for exchange splitting of the Ni²⁺ ground state in $KMnF_3$ is given by the emission spectra shown in Fig. 1. The ground state of the Ni²⁺ ion, $^3A_2$, consists of a spin triplet and an orbital singlet. If exchange interactions between Ni²⁺ and ordered Mn²⁺ spins were negligible, then the ground state should be essentially unsplit, since $KMnF_3$ is cubic, or near-
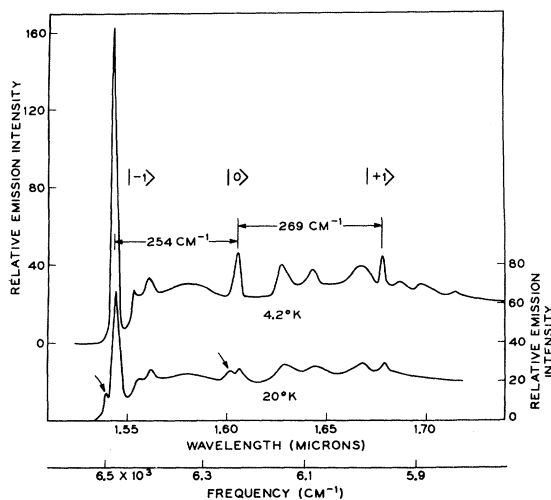
ly so.[4] We note, first, that three lines at 6479, 6225, and 5956 cm⁻¹ are quite narrow and prominent in the spectrum at 4.2°K. Second, two additional lines appear in the 20°K spectrum each displaced by the same amount (~15 cm⁻¹) to the high-energy side of the lines at 6479 and 6225 cm⁻¹. Third, the 15-cm⁻¹ splitting in the higher energy doublet (near 6500 cm⁻¹) is also seen in absorption at 1.6°K. Therefore, the two temperature-dependent lines arise from an emitting state slightly above the emitting state for the 4.2°K spectrum. Of greater significance, however, is that the presence of the two temperature-dependent lines implies that the transitions at 6479 and 6225 cm⁻¹ both represent zero-phonon, zero-magnon transitions to the $^3A_2$ state of the Ni²⁺ ion, i.e., the ground state is split by the exchange field arising from ordered Mn²⁺ spins. (It would be difficult to account for the observed intensity ratio of the two temperature-dependent lines if the two lines near 6225 cm⁻¹ were vibronic sidebands of the two lines near 6479 cm⁻¹.) Since such an interaction would completely remove the spin degeneracy, the third prominent line is assigned to the third spin component of the Ni²⁺ ground state. The transitions identify the states according to M_S, the component of spin along the direction of magnetization. Our choice of sign for the $|\pm1\rangle$ states is arbitrary. Behavior similar to $KMnF_3$ is observed for cubic $RbMnF_3$. In uniaxial MnF_2 the additional temperature-dependent lines are not seen, there being only one emitting state up to 20°K, but transitions to the $|M_S\rangle$ states are strongly polarized (Fig. 2), to $|\pm1\rangle$ with π polarization and to $|0\rangle$ with σ. At 77°K, the spectra are very broad and almost featureless. There is some structure near the transition to $M_S = 0$, but none around the transitions to $M_S = \pm1$. Furthermore, emission near $|-1\rangle$ is very weak. We suggest that at this temperature (above the Néel temperature for MnF_2) the exchange field has vanished, and the levels of the Ni²⁺ ground state have collapsed about $M_S = 0$.[5]

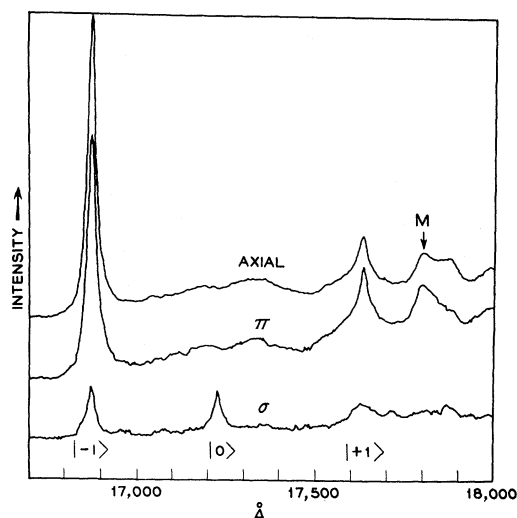An energy-level diagram showing the lowest levels of Ni²⁺ in the ordered state of the three

FIG. 1. Emission spectra of Ni²⁺ (0.01%) in $KMnF_3$ at 4.2 and 20°K.

FIG. 2. Polarization of the emission from Ni^{2+} (0.2%) in MnF_2 at 1.5°K.

FIG. 3. Energy level diagram for the lowest levels of Ni^{2+} in MnF_2, $KMnF_3$, and $RbMnF_3$. The ground-state components are labeled by M_S, the component of spin along the direction of magnetization.

compounds is given in Fig. 3. Assuming an isotropic exchange interaction of the form $-2J\vec{S}_i \cdot \vec{S}_j$, where $S_i = 1$ for Ni^{2+} and $S_j = \frac{5}{2}$ for Mn^{2+}, values of the exchange integral J_{Mn-Ni} were computed from the splittings shown in Fig. 3.[6] We have assumed that interactions are important only between Ni^{2+} and the six nearest Mn^{2+} neighbors in the perovskite compounds, and the eight second-nearest neighbors in MnF_2. The resulting values for J_{Mn-Ni} are compared with corresponding values for J_{Mn-Mn}, obtained from neutron scattering, in Table I. The neglect of first-nearest-neighbor interactions in the case of MnF_2 possibly accounts for its relatively lower value of J_{Mn-Ni}/J_{Mn-Mn}. The figures for $KMnF_3$ and $RbMnF_3$ may be compared with an exchange integral of 9 cm^{-1} for a $Ni^{2+}-Mn^{2+}$ pair in $KZnF_3$,[7] and to a value of 8.2 cm^{-1} from measurements of the paramagnetic Curie temperature.[8] Our experiment does not permit us to determine the sign of J_{Mn-Ni}; however, a negative sign is obtained for Ni-Mn pairs in $KZnF_3$.[7]

We should also point out that, with the identification of the exchange-split electronic transitions, the splittings of some of the sidebands from these zero-phonon lines are identical to the zone-boundary magnon frequencies determined by inelastic neutron scattering. For example, the magnetic dipolar portion (labeled M in Fig. 2) of the sideband of the transition to the $|+1\rangle$ state of Ni^{2+} in MnF_2 is split from this transition by 55 cm^{-1}, the energy of the
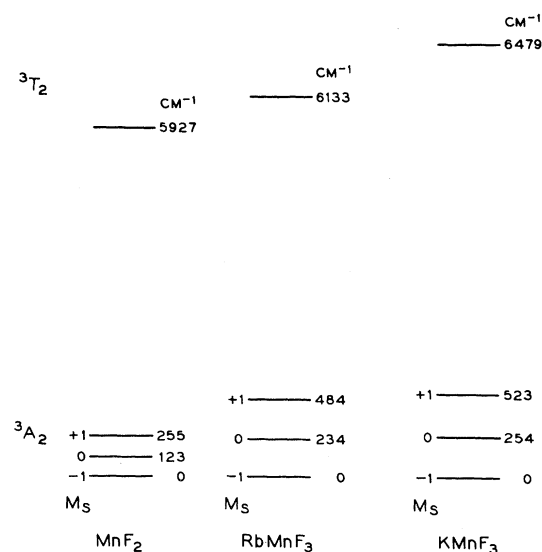
zone-boundary magnon in the $\langle 001\rangle$ direction.[9] This may be compared with the electric dipole absorption recently identified as a magnon sideband of an intrinsic optical excitation of MnF_2.[10]

Finally, energy transfer from Mn^{2+} to Ni^{2+} ions is readily seen in the excitation spectrum for Ni^{2+} emission. An absolute measurement shows the fluorescence quantum efficiency to be essentially unity when exciting the lowest three Ni^{2+} bands around 0.65, 0.8, and 1.4 μ. However, the strongest pump band for Ni^{2+} emission is the $^4T_1$ of Mn^{2+} at about 0.52 μ. For a 1% Ni^{2+} concentration, this band is also nearly 100% efficient in producing Ni^{2+} emission (the total emission intensity from the $^4T_1$ band of manganese[11-13] is diminished by more

Table I. Exchange integrals for $-2J\vec{S}_i \cdot \vec{S}_j$ interaction.

	J_{Mn-Mn} (cm^{-1})	$\lvert J_{Mn-Ni}\rvert$ (cm^{-1})	$\lvert J_{Mn-Ni}/J_{Mn-Mn}\rvert$
MnF_2	-1.22[a]	3.2	2.6
$KMnF_3$	-2.5 ± 0.3[b]	8.7	3.5
$RbMnF_3$	-2.36 ± 0.2[c]	8.1	3.4

[a]Ref. 9.

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

than two orders of magnitude by the presence of 1% Ni^{2+} ions). Ni^{2+} emission may also be excited through the Mn^{2+} bands near 4300 Å, but these are superimposed on a $^3T_1$ band of Ni^{2+}. Particularly interesting is the fact that the efficiency of $Mn^{2+} \rightarrow Ni^{2+}$ energy transfer is high even for very low Ni^{2+} concentration. For example, in MnF_2 containing 15 ppm Ni^{2+} ions, the quantum efficiency for Ni^{2+} emission is about 30% at 4.2°K when exciting the $^4T_1$ band of Mn^{2+}. To illustrate this figure somewhat differently, consider a sphere about each Ni^{2+} ion such that all Mn^{2+} ions within the sphere transfer their excitation to Ni^{2+}, while those outside do not. The radius of the sphere so calculated for MnF_2 containing 15 ppm Ni^{2+} ions is about 60 Å. These findings indicate that energy transport between Mn^{2+} ions is extremely long range, just as suggested previously for nickel compounds.[2]

We are grateful to C. G. B. Garrett and G. K. Wertheim for several helpful suggestions on the manuscript.

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[5]Strictly speaking, the transition to $M_S = 0$ would be expected to shift due to the disappearance of exchange splitting in the excited state. Since the frequency of this transition is approximately the same above and below the ordering temperature, we conclude that the effect of exchange on the emitting state is small.

[6]The exchange integrals were computed from the average splitting of the $|\pm 1\rangle$ states from $|0\rangle$. The slight asymmetry in these splittings ($\sim$3-4%) may be explained, at least in part, by the contribution of transverse components of the exchange field (A. Misetich and R. E. Dietz, to be published).

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ZERO-BIAS ANOMALIES IN NORMAL METAL TUNNEL JUNCTIONS

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We have investigated the current flow through thin chromium-oxide layers from 1°K to 290°K. We believe that current flows by means of a tunneling mechanism, but the dependence of the dynamic resistance of the junction on voltage and temperature is completely anomalous in terms of expected tunneling behavior. Some new results on other metal-oxide junctions strongly suggest that properties of the oxide layer are responsible for the anomaly observed by Wyatt in tantalum oxide junctions.

We have investigated the current flow through thin chromium oxide layers from 1 to 290°K. We believe that current flows by means of a tunneling mechanism, but the dependence of the dynamic resistance of the junction on voltage and temperature is completely anomalous in terms of expected tunneling behavior. The dynamic resistance at zero bias increases with decreasing temperature approximately as $\log(1/T)$ and, at fixed temperature, depends on voltage as $\log(1/V)$. In contrast to previously reported anomalies at zero bias,[1-10] which were of small magnitude and which were observed only at low temperatures, the total current in chromium oxide junctions appears to participate in the anomalous tunneling mechanism, and the anomaly has been observed from 1°K to room temperature. Some new results on other metal oxide junctions strongly suggest that properties of the oxide layer are responsible for the anomaly observed by Wyatt[1] in tantalum oxide junctions. In these cases, the