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SUPERTRANSFERRED HYPERFINE INTERACTION: PERTURBED ANGULAR CORRELATION (PAC)
OF ^{111m}Cd IN KNiF_3 , KCoF_3 , AND RbMnF_3^*

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Abstract:

The PAC of ^{111m}Cd in antiferromagnetic KNiF_3 , KCoF_3 , and RbMnF_3 has been observed. The Cd hyperfine fields are interpreted to yield fractional spin densities of the Co-F and Mn-F bond, $f_\sigma = 2.6\%$ and 3.8% respectively. The latter value disagrees with neutron diffraction values.

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Perturbed angular correlation (PAC) of gamma rays is a valuable tool for the determination of nuclear properties of radioactive isotopes.¹ In recent years it has been extensively applied to the study of extranuclear properties.² Until now, however, this technique has not been employed in what appears to be one of its most powerful applications: the study of supertransferred hyperfine structure in transition-metal salts. The PAC isomer ^{111m}Cd , for example, provides a probe with qualities not available elsewhere. It is a dipositive, diamagnetic impurity that can be detected at extremely low concentrations. In this Letter we report the time differential perturbed angular correlation spectra of ^{111m}Cd as a dilute impurity in KNiF_3 , KCoF_3 , and RbMnF_3 . Well-resolved magnetic hyperfine structure was observed in each case. This

was interpreted to yield new estimates of the fractional spin densities f_{σ} of the Co-F and Mn-F bonds. The former ($f_{\sigma} = 2.6\%$) agrees well with earlier values, but the latter ($f_{\sigma} = 3.8\%$) stands in sharp disagreement with an earlier estimate of 1.2% based on neutron diffraction data. The covalent character of the Mn-F bond, as obtained from the earlier result, was anomalously low. Our result would remove this anomaly.

The perovskites KNiF_3 ($T_N = 253.5^\circ\text{K}$) and RbMnF_3 ($T_N = 82.9^\circ\text{K}$) are simple cubic antiferromagnets (type G). KCoF_3 has the same magnetic structure, but with the magnetic transition a slight tetragonal lattice distortion occurs. Within experimental error, however, no deviation of the observed spectra from the simple cubic case (i.e., no quadrupole splitting) was found. In the following we neglect this distortion. The Cd^{2+} probe has as its nearest magnetic neighbors six transition-metal ions all belonging to the same sublattice in the antiferromagnetic state. The magnetic field induced at the site of the Cd nucleus perturbs the angular correlation of its well-known³ 150 keV - 247 keV cascade. The corresponding attenuation coefficient for a polycrystalline sample is⁴ $A_{22}G_{22}(t) = \frac{A_{22}}{5} \{1 + 2 \cos(2\pi \nu_L \cdot t) + 2 \cos(4\pi \nu_L \cdot t)\}$, where $\nu_L = g_N \beta_N H_{\text{hf}}$ is the Larmor frequency of the ^{111}Cd nucleus in the 247-keV state ($I = 5/2$, $g_N = -0.7952$ nm, $\tau_N = 84$ nsec)^{3,5} and H_{hf} is the hyperfine field.

The PAC spectra of Cd in KNiF_3 , KCoF_3 , and RbMnF_3 at 4°K are shown in Fig. 1. We include the spectrum of RbMnF_3 at 77°K . The decrease in sublattice magnetization with temperature is shown by the decrease of the Larmor frequency. The spectra were taken with a conventional fast-slow setup, described earlier.⁶ NaI(Tl) detectors ($1'' \times 1-1/2''$) were used. $^{111\text{m}}\text{Cd}$ was obtained by neutron irradiation of ^{110}CdO . After the irradiation the oxide was converted to the fluoride and subsequently melted with zone-refined KNiF_3 ,

KCoF₃, and RbMnF₃ in a Pt crucible. No dependence of the Larmor frequencies on the concentration of Cd was observed. At higher concentrations a decrease of A_{22}^{eff} was found. A concentration of 0.05 mole % Cd was chosen for KNiF₃ and KCoF₃ and 0.4% for RbMnF₃. The observed hyperfine fields at the Cd nucleus (4°K) are 105.6 (±1.5) kOe (KNiF₃) 74.4 (±1.0) kOe (KCoF₃) and 113.5 (±1.5) kOe (RbMnF₃). Since the reduced temperatures T/T_N are less than 0.05 at 4.2 K, these values for the hyperfine fields can be taken as very close to the 0 K values.

The hyperfine fields at the Cd nuclei are presumably caused by supertransferred spin densities in Cd orbitals (for general discussions of covalency and superexchange see Refs. 7 and 8). Because of the cubic symmetry, all dipole fields cancel. Similarly, spin densities transferred into p- or d-orbitals of Cd²⁺ do not contribute to the hyperfine field, except via core polarization. We neglect these contributions, since they should be much smaller than those caused by spin densities directly transferred into s orbitals of Cd²⁺.

We shall discuss the observed hyperfine fields in terms of a simple 3-atom superexchange model $\text{Me}^{++} - \text{F}^- - \text{Cd}^{++}$ ($\text{Me}^{++} = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$). It is similar to the model used by Owen and Taylor⁹ to explain the hyperfine field at an Al site in $\text{LaAlO}_3/\text{Fe}^{3+}$, measured by ENDOR. It is well known from NMR measurements^{10,11} that there are spin densities f_s, f_σ, f_π in fluorine 2s, 2p_σ and 2p_π orbitals, arising from overlap and covalency in the transition metal-fluorine bond. Since f_s is usually much smaller than the densities in p-orbitals, we consider only the effects of overlap and covalent bonding of p orbitals with Cd ns orbitals. Because of symmetry only f_σ orbitals can give nonzero contributions to $H_{\text{hf}}(\text{Cd})$ through the 180° $\text{Me}^{2+} - \text{F}^- - \text{Cd}^{2+}$ bond. The hyperfine field at the Cd nucleus is therefore proportional to f_σ , independent

of which s-orbitals of Cd are used for overlap and independent of the amount of bonding with the 5s orbital. The $Me^{2+} - F^-$ bond lengths, and presumably therefore the $Cd^{2+} - F^-$ bond lengths, are similar (2.01 Å in $KNiF_3$,¹² 2.03 Å in $KCoF_3$,¹² 2.12 Å in $RbMnF_3$ ¹³). To a good approximation the induced hyperfine fields on Cd^{2+} should be related to the fractional spin densities in the F^- 2p shell by equations of the form

$$\frac{H_{hf}(Cd \text{ in } KCoF_3)}{H_{hf}(Cd \text{ in } KNiF_3)} = \frac{\frac{1}{2} \left(\frac{\langle S \rangle}{S} \right)_{Co}}{\frac{1}{2} \left(\frac{\langle S \rangle}{S} \right)_{Ni}} \cdot \frac{f_{\sigma}^{Co}}{f_{\sigma}^{Ni}}$$

Here the different zero spin deviations have been taken into account. The spin expectation values $\langle S \rangle$ can be calculated using spin wave theory⁹ as $\langle S \rangle = S - \frac{1}{2z}$ ($z = 6$). The accuracy of this estimate is much less important here than for neutron-diffraction studies, in which an additive correction of the order of $1 - \langle S \rangle / S$ must be made in determining f_{σ} . Since f_{σ}^{Ni} is known unambiguously from NMR ($f_{\pi}^{Ni} = 0$, $f_{\sigma}^{Ni} = 3.8\%$)¹¹ we obtain for $KCoF_3$ and $RbMnF_3$

$$f_{\sigma} = 2.6\% \text{ (Co-F)}$$

$$f_{\sigma} = 3.8\% \text{ (Mn-F)}$$

The first value is in good agreement with the value $(2.4 \pm 1.0)\%$ of Thornley et al.,¹⁴ which was obtained by a detailed analysis of the fluorine super-hyperfine structure of the CoF_6^{4-} EPR spectrum.

Analyzing the ^{19}F NMR in $KMnF_3$, Shulman and Knox¹⁵ obtained for the spin densities in the fluorine 2p orbitals $f_{\sigma} - f_{\pi} = 0.35\%$. Later Walker et al.¹³ found nearly the same value (0.33%) in $RbMnF_3$. Comparing the f_{σ} value for NiF_6^{4-} ($f_{\sigma} = 3.8\%$, $f_{\pi} = 0$) and the f_{π} value for CrF_6^{3-} ($f_{\pi} = 4.9\%$, $f_{\sigma} \approx 0$) Shulman

and Knox¹⁶ suggested that the small value of $f_{\sigma} - f_{\pi}$ generally found in manganese fluoro complexes is caused by nearly complete cancellation of f_{σ} and f_{π} . However, since the measurement of the hyperfine field at the fluorine nucleus yields only the difference $f_{\sigma} - f_{\pi}$, an independent measurement must be made to determine f_{σ} and f_{π} individually. This information was obtained from neutron diffraction. Alperin¹⁷ observed in antiferromagnetic NiO a contraction of the magnetic moment distribution below the free ion value of Ni^{2+} . A similar situation was observed by Nathans et al.¹⁸ who determined the moment distribution in antiferromagnetic MnF_2 . These effects, which are caused by the covalency of the transition metal-ligand bond, were related to the fractional spin densities f_s , f_{σ} , and f_{π} in a theory developed by Hubbard and Marshall.¹⁹ Using this theory Alperin obtained for NiO $(f_{\sigma} + f_s) = 6.0\%$, which reduces to 4.1% after correction²⁰ for zero spin deviation. Nathans et al.²¹ reported for MnF_2 $(f_s + f_{\sigma} + 2f_{\pi}) = 3.3\%$. Using a different approach Nathans²¹ determined the fractional spin densities in antiferromagnetic MnO by measuring the total intensity of the low angle magnetic powder diffraction peaks ($f_s + f_{\sigma} + 2f_{\pi} = 3.3\%$). Applying this technique to NiO (and MnO) Fender et al.²⁰ found in both cases satisfactory agreement with the earlier reported values. Two conclusions were drawn from these results:

1. Using $f_s = 0.5\%$ and $f_{\sigma} - f_{\pi}$ obtained by NMR, Nathans²¹ calculated for MnF_2 $f_{\sigma} = 1.2\%$. Mn^{2+} was believed to have an abnormally low covalent character.
2. Comparing $f_{\sigma} + f_s$ in KNiF_3 (4.3%, NMR) and NiO (4.1%, neutron diffraction) and $f_s + f_{\sigma} + 2f_{\pi}$ in MnF_2 (3.3%) and MnO (3.3%), both obtained by neutron diffraction, oxygen and fluorine were believed to be equally covalent.

We seriously question both conclusions. The value of f_{σ} (3.8%) for the Mn-F bond, reported in this Letter suggests that Mn^{2+} is as covalent as Ni^{2+} .

While the details of interpretation of all the methods for determining f_{σ} are subject to question on the basis of oversimplification, it would be very difficult to reconcile the relatively large hyperfine field at Cd in RbMnF_3 with an f_{σ} value as low as 1.2%. It appears in fact that in all cases (NiO , MnO , MnF_2) neutron diffraction yields spin densities lower than expected from hyperfine-interaction studies. A similar observation was made by Tofield and Fender,²² who determined the spin densities of oxygen in LaCrO_3 by neutron diffraction, finding $f_{\pi} = 1.6\%$, which is a factor of three lower than the resonance results. Until this systematic discrepancy is definitively resolved, conclusion (2) above is in doubt. It should also be noted that Henning's²³ analysis of the hyperfine structure of Mn^{2+} , based on an observation by Van Wieringen,²⁴ yields results that flatly contradict both conclusions (1) and (2): i.e., in fluorides Mn^{2+} is about 5% covalent, and in oxides it is distinctively more covalent.

Covalency is a basic (albeit rather qualitative) concept in chemistry, and fractional spin density parameters play a crucial role in the theory of superexchange. Because the hyperfine field at the anion nucleus is determined by the difference $f_{\sigma} - f_{\pi}$, no further information can be expected from NMR, EPR, or ENDOR investigations of the ligand (F^-) hyperfine structure. It seems preferable to measure the hyperfine field at a cation nucleus. Since paramagnetic cation - diamagnetic cation (180°) superexchange is σ bond specific, these measurements are probably more suitable than the measurement of the hyperfine interaction of the magnetic ion itself. By using ^{111}mCd as a diamagnetic probe, one can take advantage of the high sensitivity of the PAC method to study hyperfine fields at Cd probe nuclei at very small concentrations in antiferromagnetic lattices. This should provide new, independent data to help resolve the existing spin-density discrepancies.

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FOOTNOTES AND REFERENCES

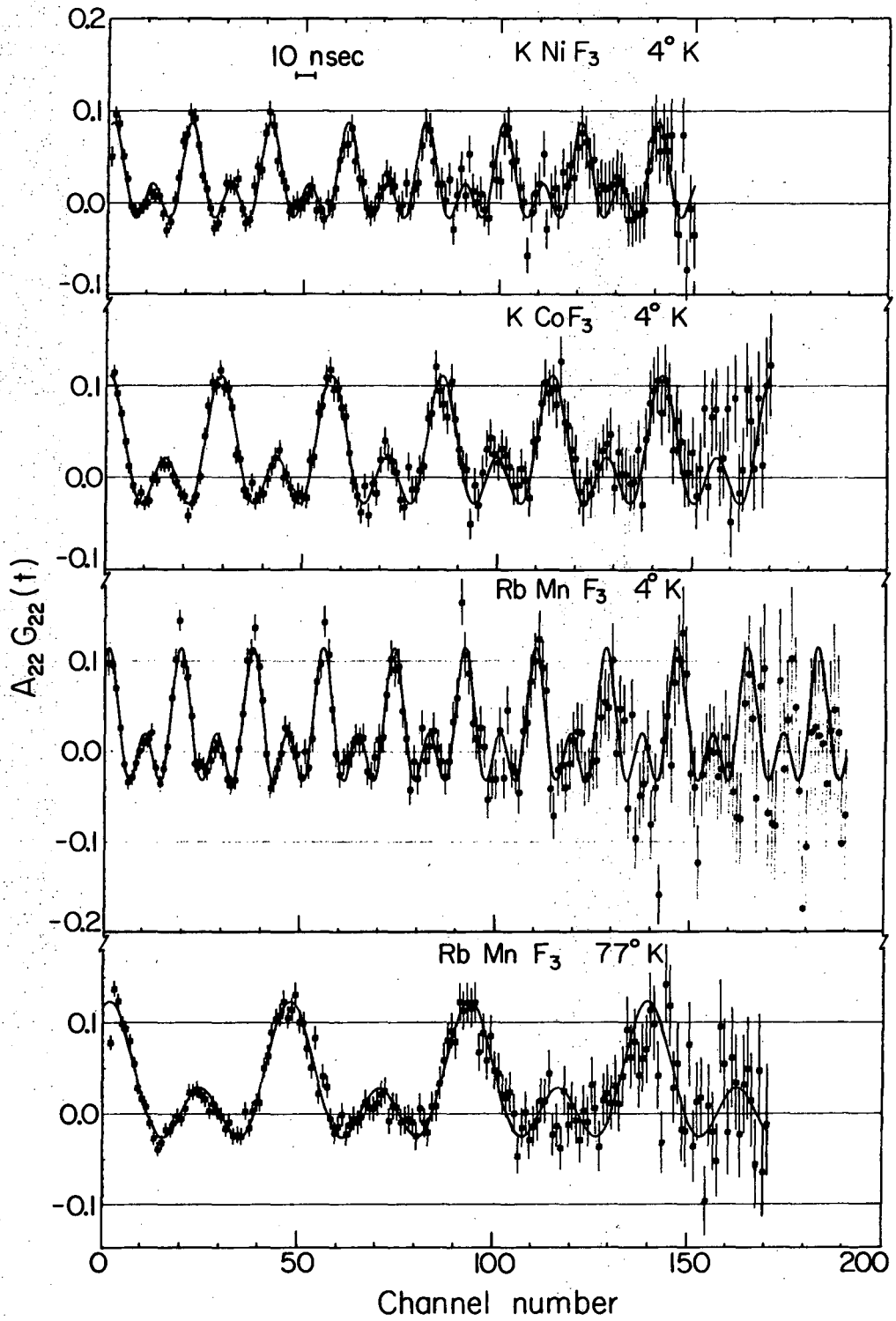
* Work performed under the auspices of the U. S. Atomic Energy Commission.

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FIGURE CAPTION

Fig. 1. Time differential PAC spectra of ^{111m}Cd in antiferromagnetic KNiF_3 , KCoF_3 , and RbMnF_3 .



XBL 734-2591

Fig. 1

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