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Direct NMR measurements of the ^{19}F-Mn transferred hyperfine interaction in Mn:PbF$_2$

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The ^{19}F-Mn transferred hyperfine interaction $\tilde{A}$ in Mn:PbF$_2$ has been determined by direct observation of the NMR of ^{19}F nuclei nearest neighbor to the Mn^{2+} impurity. The angular dependence of the NMR of three inequivalent sites was studied for applied fields in the (110) plane and was fitted with the values $A_s = 33.82$ MHz and $A_p = 7.82$ MHz. The NMR was unobservable for $T > 2$ K, suggesting rapid electronic spin relaxation. For $T < 1.5$ K, NMR was observed in the eigenstates of the Mn^{2+} with $S_z = \frac{5}{2}$ and $\frac{3}{2}$; the linewidth ΔH became temperature independent and probably inhomogeneously broadened, with a pronounced angular variation.

I. INTRODUCTION

The study of the electron-nuclear interaction between paramagnetic impurities and near-neighbor (NN) nuclei in solids has involved the application of several experimental techniques. The interaction Hamiltonian,

$$\mathcal{H}_{\rm int} = \sum_{\alpha,\beta} S_\beta A_{\alpha\beta} I_\alpha \ , \qquad (1)$$

perturbs both the electronic and nuclear energy levels, and quantitative determination of the transferred hyperfine tensor $\tilde{A}$ can be obtained from EPR, ENDOR, or NN-NMR studies. For example, if the interaction manifests itself as well-resolved superhyperfine structure, $\tilde{A}$ can be determined directly from the impurity EPR spectrum.[1]

In the absence of well-resolved superhyperfine structure the ENDOR technique can provide high-resolution spectra of the rf transitions from which $\tilde{A}$ can be derived.[2] Experimentally ENDOR is somewhat complicated as the technique involves monitoring the partially saturated EPR spectrum while simultaneously applying rf power at the NMR frequency of the NN nuclei; consequently, both EPR and NMR spectrometers are required.

An alternative, and perhaps simpler, approach in the case of unresolved superhyperfine structure in the impurity EPR is the NN-NMR experimental technique in which the NMR of nuclei NN to the impurity is observed directly. The technique was first used in insulators to study proton NN-NMR in Yb^{3+}YES,[3] and ^{19}F NN-NMR in MnF$_2$ doped with various magnetic and nonmagnetic impurities.[4] The method has subsequently been employed to study both proton NN in rare-earth doped YES[5] and ^{19}F NN in rare-earth-doped CaF$_2$,[6] and ^{19}F NN in Mn^{2+}: FeF$_2$.[7,8]

The conditions for observing NN-NMR are rather stringent. If the correlation frequency $1/\tau_c$ for the fluctuation of the impurity spin S_z is comparable with the nuclear Larmor frequency ω_0, broadening of the NN-NMR of the order of $A = A_{zz}$ will result. Since A may be rather large, the NN-NMR is unobservable in this case, and becomes observable only in the limits of either very long, or very short τ_c. In the diamagnetic host, the long-τ_c limit is usually found at low enough temperatures, such that $\omega_0 \tau_c >> 1$. In this limit, the election spin is effectively static, and the NN-NMR shift corresponds to $S_z = M$, where M is any of the $(2S+1)$ eigenvalues of S_z. The NN-NMR linewidth is then due to the nuclear dipole-dipole interaction. At higher temperature, increased electronic relaxation rates contribute a lifetime broadening $\delta\omega = 1/\tau_c$ and the NN-NMR disappears. This is to be contrasted with the observed NMR shifts in magnetically dense materials, where it is usually found that $A\tau_c << 1$, and the shift is proportional to the time average of S_z, $\langle S_z \rangle$.[9] In this case the linewidth is given by $\delta\omega \propto A^2 \langle \delta S_z^2 \rangle \tau_c$, where $\langle \delta S_z^2 \rangle$ is a temperature-dependent factor describing the population of the various S_z levels.[10]

The present work was motivated by the need to know the full NN hyperfine tensor $\tilde{A}$, in order to compare theory with experiment in the ^{19}F nuclear relaxation in Mn^{2+}:PbF$_2$ at high temperatures. This work is reported in a companion paper, immediately preceding the present work in this volume.[11]

Previously Evora *et al.*[12] have reported the EPR spectrum for Mn^{2+} in Mn:PbF$_2$. The superhyperfine structure of the spectrum was not well resolved, and could be measured only along [100]. Therefore, only the quantity $(\frac{1}{3}A_\parallel^2 + \frac{2}{3}A_\perp^2)^{1/2} = 25 \pm 1$ MHz could be determined. We have chosen the NN-NMR technique for further investigations in this system, since it seems most straightforward, particularly in the case of partially resolved ^{19}F hfs. The NN-NMR data have been found to be in serious disagreement with the EPR result, as will be discussed later.

II. ANGULAR VARIATION OF THE NN-NMR SPECTRUM

Since the NN-NMR spectrum clearly shows the Mn^{2+} reside in cubically coordinated lattice sites with eight NN ^{19}F, we assume the Mn^{2+} enter the PbF_2 structure substitutionally for Pb^{2+}. Another possible location is the normally vacant body centered position. In the latter case, charge neutrality requires the introduction of two F^- interstitial ions, but as cubic symmetry of the local Mn^{2+} environment is apparently preserved, the charge compensation cannot be attained locally.

In general, nine components of $\tilde{A}$ are required to specify the interaction of Eq. (1), but $\tilde{A}$ has axial symmetry about the bond axis connecting I and S.[1] As illustrated in Fig. 1, these bonds lie along the four equivalent [111] directions in PbF_2, so in a coordinate system with the Z axis colinear with [111], $\tilde{A}$ may be specified by two components, $A_{\parallel}$ and $A_{\perp}$. Alternatively, $\tilde{A}$ may be expressed as a scalar (A_s) plus a dipolar (A_p) term, where

$$A_s=\tfrac{1}{3}(A_{\parallel}+2A_{\perp})$$

and

$$A_p=\tfrac{1}{3}(A_{\parallel}-A_{\perp}) \ . \tag{2}$$

If the external magnetic field H_0 is applied in a (110) plane, there can be, at most, three inequivalent ^{19}F sites. H_0 may be applied parallel to all three symmetry axes of the crystal by rotating the sample about the [110] axis perpendicular to the (110) containing H_0. For H_0 applied along [100], all ^{19}F are equivalent. For H_0 along [110], the type 2 and 3 sites are equivalent, and for H_0 along [111], the type 1 and 3 sites are equivalent.

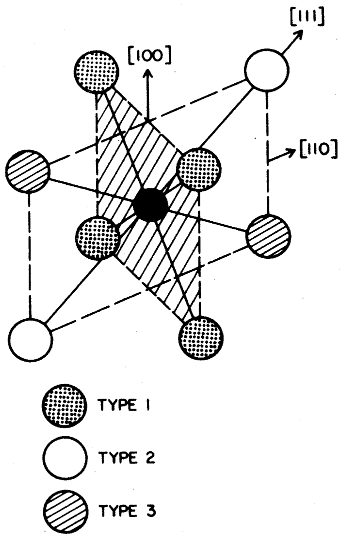

FIG. 1. In the NN-NMR experiment, H_0 is applied in the unshaded (110) plane making an angle θ with respect to the [111] direction. This admits, at most, 3 inequivalent sets of ^{19}F nuclei. Type 1 sites lie in the shaded (110) perpendicular to the plane (unshaded) containing H_0. Type 2 and 3 sites lie along the [111] in the (110) that contains H_0.

The total field at the NN nucleus is given by the vector sum of $\vec{H}_0$ and the hyperfine field $\vec{H}_{hf}=\sum_{\beta}A_{\alpha\beta}S_{\beta}$, where $\tilde{A}$ is expressed in field units. The resonance condition is

$$\omega_0=\gamma|\vec{H}_{tot}|=\gamma|\vec{H}_0+\vec{H}_{hf}| \ . \tag{3}$$

Solving Eq. (3) for the geometry described above, assuming that, in the long-τ_c limit at low T, $S_z=M$, and $\langle S_x\rangle=\langle S_y\rangle=0$, we find for the type 1 nuclei

$$H_0=-[A_sS_z+A_pS_z(\cos^2\theta-1)]+\left\{\frac{\omega_0^2}{\gamma^2}-A_p^2S_z^2\cos^2\theta(1+\cos^2\theta)\right\}^{1/2} , \tag{4}$$

where θ is the angle between $\vec{H}_0$ and [100]. For type 2 (3) nuclei

$$H_0=-[A_sS_z+A_pS_z(3\cos^2\theta-1)]+\left\{\frac{\omega_0^2}{\gamma^2}-9A_p^2S_z^2\sin^2\theta\cos^2\theta\right\}^{1/2} , \tag{5}$$

where $\theta(\theta+70.52°)$ is the angle between $\vec{H}_0$ and [111].

III. EXPERIMENTAL APPARATUS AND PROCEDURES

The experiments were performed using a high-frequency broadband cw NMR bridge spectrometer at a frequency of 125 MHz, at $T=1.3$ K in magnetic fields up to 16 kOe. The NMR spectrometer has been described elsewhere.[13] The resonator was a coil-air capacitor design with $Q\simeq 1000$ at low temperatures. The sample was a single-crystal specimen of Mn:PbF_2 containing 0.1 mole % of Mn^{2+}. It was oriented to within 1° with a rotation axis parallel to [110]. H_0 was applied in the (110) plane perpendicular to the axis of rotation. Both the sample and resonator were immersed in the liquid in a Dewar of pumped He, and a carbon glass resistor was used to monitor the temperature.

IV. RESULTS

The ^{19}F NN-NMR was unobservable for temperatures in excess of 2 K, appearing rather suddenly as the temperature was lowered. Since an electronic T_1 of 1 μsec contributes a lifetime broadening of the NN-NMR of 40 Oe, a T_1 only somewhat shorter than this can explain the disappearance of the NN-NMR. This observation is to be compared with the Mn^{2+} electronic relaxation measured in Mn:SrF$_2$ and Mn:BaF$_2$, in which a direct ($\propto T$) and Raman ($\propto T^5$) process are observed.[14] Although the electronic τ_c^{-1} in Mn:PbF$_2$ is considerably faster than the Raman contributions observed at the same temperature in the other fluorites, it is, perhaps, not unreasonable, considering the more covalent character of PbF$_2$. At lower temperatures, around $T = 1.3$ K, the linewidth becomes temperature independent, and apparently inhomogeneous in origin. Interestingly, the inhomogeneous width is extremely angular dependent, with the narrowest widths of ~50 Oe occurring at extremal points ($A_{\parallel}$ and $A_{\perp}$), and broadening to roughly 300 Oe in between. This suggests that the inhomogeneity is not in the magnitude of the interaction, but may be due to a variation in the Mn–F bond directions.

In Fig. 2 we show both the measured and calculated resonance fields for $S_z = \frac{5}{2}$ for type 1, 2, and 3 ^{19}F NN-NMR resonances. The curves with maximum excursion correspond to the type 2 and 3 resonances and are displaced from each other by 70.52°, the angle between the equivalent [111]. The curve with smaller excursion corresponds to the type 1 nuclei. The resonance line of the type 1 ^{19}F is split slightly as the maximum shift (minimum resonance field) is approached. This effect is produced by a slight misalignment of the sample which causes the four F^- out of the plane containing H_0 to form two sets of inequivalent *pairs* of nuclei. No splitting is observed for the type 2 and 3 resonances, which arise from pairs of nuclei, and are therefore necessarily equivalent.

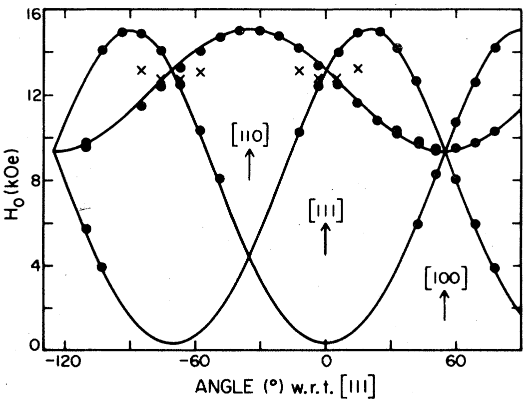

FIG. 2. Angular dependence of the ^{19}F NN-NMR resonance fields. H_0 is applied in the (110) plane making an angle θ with respect to [111]. The filled circles are resonant fields corresponding to $S_z = \frac{5}{2}$, the ×'s are for $S_z = \frac{3}{2}$. The solid curves are the predictions of Eqs. (4) and (5) with $A_s = 33.82$ MHz, $A_p = 7.82$ MHz, and $S_z = \frac{5}{2}$.

For the type 2 (3) nuclei, the minimum shift is observed when H_0 is perpendicular to the bond axis of the pair. Hence a maximum resonance field of 15 kOe is observed when θ or $\theta + 70.52° = \pi/2$. From Eq. (5) we find, using $S_z = \frac{5}{2}$, that

$$A_{\perp} = A_s - A_p = \frac{\omega_0 - \gamma H_0}{2\pi S_z} = 26.00 \text{ MHz} . \qquad (6)$$

Similarly, a minimum in the resonance field occurs when H_0 is parallel to the bond axis which occurs for $\theta(\theta + 70.52°) = 0$ and π. Unfortunately, the type 2 and 3 resonances for $S_z = \frac{5}{2}$ are shifted so low in field as to be unobservable. However, resonances corresponding to $S_z = \frac{3}{2}$ were observed (×'s in Fig. 2) with a minimum resonance field of 12.7 kOe. Thus, using $S_z = \frac{3}{2}$ in Eq. (5), we obtain

$$A_{\parallel} = A_s + 2A_p = \frac{\omega_0 - \gamma H_0}{2\pi S_z} = 49.47 \text{ MHz} . \qquad (7)$$

Solving Eqs. (6) and (7) for A_s and A_p yields $A_s = 33.82$ MHz and $A_p = 7.82$ MHz. The curves in Fig. 2 are obtained from Eqs. (4) and (5) using these values of A_s and A_p.

It is interesting to compare our results with those determined by EPR of Mn^{2+} in the isostructural compound CaF$_2$.[15] The latter results are $A_s = 26.0$ and $A_p = 8.4$ MHz. It is surprising that A_s for Mn:PbF$_2$ is so much larger than in Mn:CaF$_2$ since the PbF$_2$ lattice is larger than that of CaF$_2$. It is usually found that A_s is inversely proportional to approximately the sixth power of the internuclear separation.[16,17] Even allowing for lattice relaxation effects,[4] which one would expect to be larger for Mn:PbF$_2$, this is an unexpected result.

Serious disagreement exists between the present measurements and those of Evora.[12] Since we have unambiguously identified the types 1, 2, and 3 ^{19}F NN's, and followed their complete angular dependence, we feel the present results are the correct ones. However, we notice that the EPR result quoted for [100] is extremely close to our result for $A_{\perp}$. This leads us to speculate that Evora may have mistaken the spectra along [110] for that along [100], and that angular-dependent broadening mechanisms, such as those observed in the NN-NMR, may have broadened the shfs in all other directions, including [100]. This could easily have happened, since we have found that orientation of single crystals of PbF$_2$ using x-ray diffraction methods is not simple. Unless extreme care is taken in the preparation of the surface, very poor Laue patterns result, which could have led to an improper identification of the sample alignment.

V. CONCLUSION

We have used the technique of NN-NMR to determine the full hyperfine tensor $\tilde{A}$ between the Mn^{2+} impurity in Mn:PbF$_2$ and its nearest-neighbor ^{19}F neighbors. The data clearly show that the impurity occupies a cubic site with eightfold ^{19}F coordination. The interaction is found to be similar to that found in Mn^{2+}:CaF$_2$, but in serious disagreement with that determined by an EPR measurement in Mn:PbF$_2$. A probable reason for the error in the EPR study is offered.

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