NMR of Nuclei near a Paramagnetic Impurity in Crystals*

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We report a new experimental NMR technique of wide applicability wherein the NMR of nuclei at crystalline sites near a localized paramagnetic impurity is directly observed. We find this method useful in determining electron-nuclear interactions and crystal structure, and as a site-selective probe of spin lattice relaxation, spin diffusion, and dynamic polarization processes for nuclei. We have applied this technique to $Y(C_2H_5SO_4)_3 \cdot 9H_2O$ doped with Yb^{3+} and Nd^{3+}, $CaF_2:Eu^{2+}$, and $NH_4Cl:Cu^{2+}(2H_2O)$.

For diamagnetic crystals containing abundant nuclear spins and dilute concentrations of paramagnetic ions, we have directly observed discrete nuclear magnetic resonances of nuclei near the paramagnetic ion. In $Y(C_2H_5SO_4)_3 \cdot 9H_2O$ (YES) doped with Yb^{3+} or Nd^{3+} ions, these *near-proton* resonances are shifted in field away from the usual *bulk-proton* resonance primarily by the dipolar field of the rare-earth ion, which is effectively static. An essential condition for observation of these spectra in this static limit is $\nu_n \gg \tau_c^{-1}$, where ν_n is the Larmor frequency of the protons and τ_c is the correlation time of $S_z(t)$ for the ion. This may be contrasted with the paramagnetically shifted NMR lines of liquids,[1] magnetically concentrated crystals,[2] or metals,[3] where the observed nuclear resonances are shifted by the *time-averaged* interaction of the electron spin or ion and the nuclei. The condition $\nu_n \gg \tau_c^{-1}$ is found to be well satisfied, e.g., for our experiments on YES:Yb at $\nu_n = 70$ MHz and below $T = 3.8°\text{K}$, where $\tau_c \simeq T_{1e} \geq 10^{-4}$ sec, and it is no doubt satisfied for many other dilute paramagnetic systems at liquid-helium temperature.

Figure 1 shows the immediate surroundings of the rare-earth site in YES. The positions of all atoms but hydrogen have been determined by x-ray analysis for pure YES.[4] Nine waters of hydration directly surround the rare-earth ion, and two of the nearest ethyl sulfate protons are shown; the proton positions have previously only been estimated by chemical arguments.[5] The nearest protons are about 3 Å from the ion; hence the predicted magnetic dipolar field at these protons is several hundred gauss, giving rise to a shift in their resonant field.

Using a high-sensitivity NMR spectrometer,[6] we have been able to detect these impurity-shifted resonances and identify them with particular proton sites. The derivative NMR spectrum for a 250-mg YES:1.6% Yb crystal is traced in Fig. 2. The external magnetic field H was aligned carefully along the crystal c axis ($\theta = 0$) in order to make many of the near-proton sites equivalent; for example, all six *H1W7* protons. Indeed, as little as 0.1° misalignment can be detected with this spectrum. For this crystal we have analyzed the shifts of the near-proton resonances using a simple dipolar field model, which predicts for the resonant field

$$H = (H_0^2 - h_\rho^2)^{1/2} \mp h_z, \tag{1}$$

where h_z and h_ρ are the orthogonal cylindrical components of the impurity dipolar field for the impurity moment aligned parallel (−) or antiparallel (+) to the external field, and $H_0 = h\nu_n / g_n\beta$. With this expression, we have determined both h_z and h_ρ from a frequency dependence ($21 < \nu_n < 70$ MHz) of the near-proton spectrum at $\theta = 0°$. The corresponding radii are tabulated in Table I for the nearest protons.

Several interesting observations can be made from these data. The measured splitting for

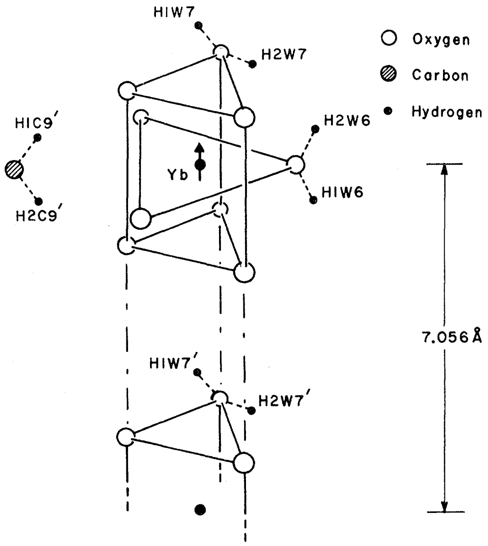

FIG. 1. Local environment of Yb^{3+} in yttrium ethyl sulfate.

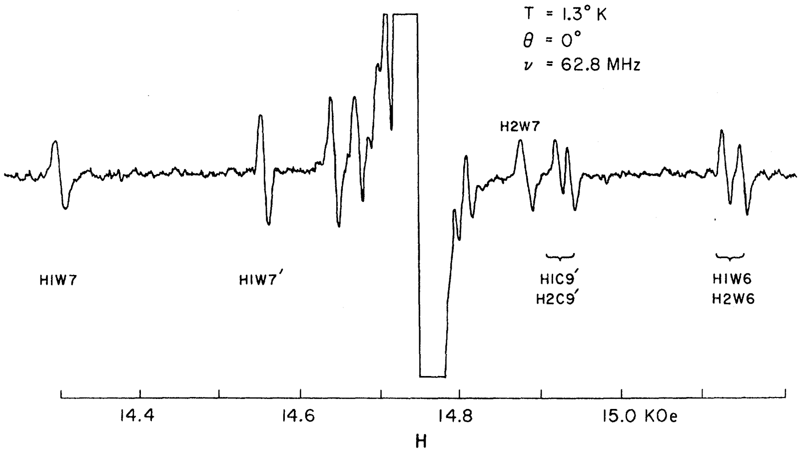

FIG. 2. Near-proton NMR spectrum of YES:1.6% Yb showing discrete resonances for protons near a Yb^{3+} ion. The bulk-proton resonance is off scale at 14.75 kOe with an intensity about 10^3 times those of the near protons.

H1W6 agrees quite well with that predicted by using a point dipole field for the Yb ion and the oxygen positions determined from x-ray analysis. This agreement strongly indicates that the scalar interaction between the Yb ion and midplane water protons is small; indeed it was too small to be obtained in these investigations. Also we find that positions of the *W7* protons, as determined from the above analysis, are somewhat different from those based on x-ray data and less certain chemical arguments. Another notable result of our experiments is that the *W7* water orientations are measurably different for Yb^{3+} and Nd^{3+} sites. Finally, the two doublets at 15.15 and 14.93 kOe are due to equivalent *H1W6, H2W6* protons and nearly equivalent *H1C9, H2C9* protons, respectively. These doublets[7] are split primarily by the magnetic dipolar interaction between the two equivalent protons. The measured splitting of 22.3 ± 0.5 Oe for the highest-field doublet corresponds to a proton-proton distance of 1.56 Å.

A striking feature of the near-proton technique is displayed in the *H1W7* and *H2W7* resonances. These resonances are located on opposite sides of the main line and are split by 600 Oe even though they originate from the *same* water molecule. Thus the near-proton spectrum is extremely sensitive to nuclear positions and therefore can be a useful tool for determining the crystal structure once the form of the electron-nuclear interaction is known. Conversely, for crystals where the structure is determined by another method, the near-proton method may be used to find the precise form of the electron-nuclear interactions. While this information may also be gained via electron-nuclear double resonance (ENDOR) techniques,[8] our NMR method is applicable even where the EPR is weak or unobservable. For YES:Yb, the extremely weak EPR transition is not amenable to ENDOR studies. We have also applied our technique to F^{19} in $CaF_2:Eu^{2+}$ and find that the near-fluorine spectrum[9] is simpler to interpret than the corresponding ENDOR spectrum.[10] Finally, a readily obtainable frequency dependence of the near-nuclei spectrum may provide additional information about the electron-nuclear interaction, similar to that acquired using Eq. (1).

TABLE I. Distances between the Yb site and the three nearest protons, assuming a point-dipole model.

Proton site	r_{meas} (Å)	r_{calc} [a] (Å)
H1W6	3.19	3.20
H1W7	2.97	3.10
H2W7	3.14	3.04

[a] Estimated from x-ray data and chemical arguments of Ref. 5.

Aside from a detailed determination of the proton positions, we have sucessfully extended our near-proton technique to the study of nuclear relaxation in YES:Yb. It is widely assumed that the nuclei in such paramagnetically doped diamagnetic crystals relax through fluctuations in the impurity dipolar field. The basic relaxation model originally proposed by Bloembergen[11] is a simplified two-step process whereby the near nuclei relax to the lattice through the paramagnetic ion, and the bulk nuclei thermalize via spin diffusion. Direct observation of the near-proton spectrum has afforded us a new tool for studying the microscopic dynamics of the actual nuclear relaxation process.

Specifically, we have measured (a) the relaxation to thermal equilibrium of *particular* near-proton resonances after rf saturation and (b) the effect on near protons of saturation of the bulk-proton line. An unexpected result of our studies is that nearly all of the near-proton lines, including many well-resolved from the main line, are in strong thermal contact with the bulk protons. In particular, our data for YES:Yb show that spin-diffusion processes are dominant for all but the very nearest protons, suggesting that the so-called diffusion barrier between bulk and near protons has little or no significance in this crystal. We find it is further possible to distinguish experimentally not only a temperature-independent Bloembergen-type spin diffusion resulting from a small overlap of the near-proton resonances, but also a temperature-dependent spin diffusion induced by fluctuations in the impurity dipolar field.[12]

To illustrate simply the process of direct relaxation of a near proton to the ion, we present in Fig. 3 the temperature dependence of the *H1W7* resonance. These data were taken at $H_0 \simeq 5$ kOe, where the Yb^{+3} electron relaxation rate T_{1e} has been recently measured.[13] The simple two-spin dipolar model predicts a nuclear relaxation rate[14]

$$T_{1d}^{-1} = (h_\rho/H)^2 T_{1e}^{-1}\,\mathrm{sech}^2(g_\parallel \beta H/2kT). \qquad (2)$$

This predicted rate for *H1W7* is the smooth curve plotted in Fig. 3. Notice that there is no curve fitting involved here since T_{1d}^{-1} is determined by the measured $T_{1e}^{-1} = 0.0135T^9$, the magnetic field, and the measured radial component of the dipolar field. The relaxation of this near proton is thus explained quite well by the simple two-spin dipolar model. Relaxation rates of other near protons are found to exhibit in addition the characteristics of spin-diffusion processes, and these data will be reported in detail later.

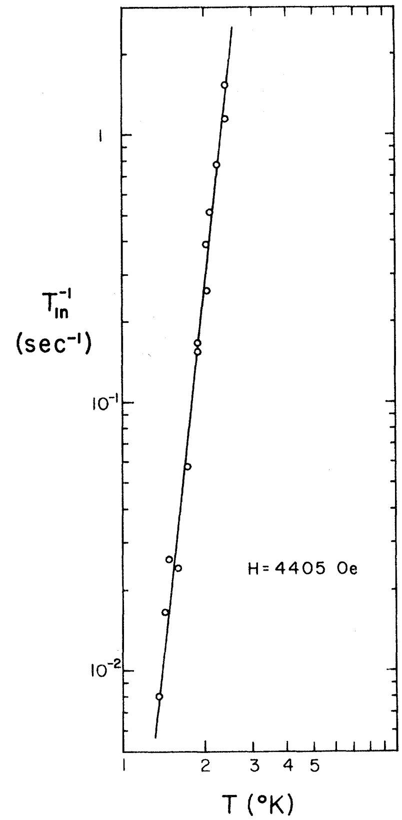

FIG. 3. Observed recovery rate at 21 MHz of *H1W7* protons in YES:Yb after rf saturation. The solid line is from Eq. (2), using T_{1e} from Ref. 13 and h_ρ measured in this work. The exceptional agreement between theory and experiment is probably the first microscopic verification yet attained for the dipolar relaxation model.

In conclusion, we have found near-nuclei magnetic resonance to be useful in the determination of crystal structure within the unit cell and as a microscopic probe of a very general relaxation process. It is expected that these methods will apply to a variety of other crystals, both simpler and more complicated than the ethyl sulfates. We have also observed discrete near-proton resonances in the cubic host $\mathrm{NH_4Cl{:}Cu^{2+}(2H_2O)}$, where the protons near the copper ion are split up to 1200 Oe away from the bulk-proton NMR, and this splitting is partially attributable to an electron-nuclear scalar interaction.[9] We feel it would be useful to study the near-nuclei spectrum in a wide variety of other materials, e.g., doped semiconductors, metals and alloys with localized magnetic impurities, biological systems of structural interest, and crystals where the electron paramagnetic resonance cannot be observed directly. Finally, we mention that this technique has been applied by us to study the details of dynamic nuclear polarization processes in YES:Yb by optical pumping.[15]

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Interpretation of Inelastic Neutron-Scattering Observations in bcc Solid and Superfluid ^{4}He

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Recent inelastic neutron scattering observations on the bcc phase of solid ^{4}He are interpreted as showing (i) substantial interference between the one-phonon peak and the multiphonon background, due to strong phonon interaction processes; and (ii) a Debye-Waller factor, extracted by use of first-moment sum rules, which closely resembles the structure of superfluid ^{4}He. We discuss implications of this resemblance for the ground-state wave functions of crystalline and superfluid helium.

Within the past year, extensive inelastic neutron scattering observations have been made[1] on large single crystals of solid ^{4}He in the bcc phase. The scattering cross sections at small momentum and energy transfers are interpretable in the standard way as yielding phonon spectra consistent with expectations from theory and from other experiments. However, at larger momentum transfers certain unusual features were found which have not been explained and which have attracted considerable interest. One way to describe the anomaly is[1] that when the magnitude of the momentum transfer $\vec{Q}$ approaches $1.6(2\pi/a)$, extra intensity (as much as 4 times larger than expected from one-phonon scattering) is observed near an energy transfer of 1.4 meV. When stated in this way, there is a temptation to suspect[1] the anomaly as evidencing a nonphonon elementary excitation in the crystal, perhaps a vacancy or other defect, or some localized yet cooperative excitation. An alternative description of the same phenomenon, which prejudices its interpretation rather differently, is that the scattering cross section exhibits a peak whose position, shape, and height vary significantly from a point in one zone of reciprocal space to a translationally equivalent point in another zone. The latter terminology offers more promise for explanation within the conventional phonon basis of lattice dynamics. It is such a possibility which we wish to explore further in this note.[2]

The inelastic neutron scattering cross section from a Bravais lattice is proportional to the density autocorrelation function,

$$S(\vec{Q},\omega) = S^{(1)}(\vec{Q},\omega) + \text{background}, \qquad (1)$$

where the one-phonon portion $S^{(1)}$ is well known to be given in the harmonic approximation by

$$S^{(1)}(\vec{Q},\omega) \cong e^{-2W(\vec{Q})} \sum_{\vec{k},\lambda} \Delta(\vec{Q}-\vec{k})\pi\delta(\omega-\omega_{\vec{k}\lambda}) \times \frac{(\vec{Q}\cdot\vec{e}_{\vec{k}\lambda})^2}{M\omega_{\vec{k}\lambda}}, \qquad (2)$$