Direct measurement of the lattice and impurity components of the spin-lattice relaxation of quadrupole nuclei

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A suppression of the impurity component of the nuclear spin-lattice relaxation (a new effect) and also a separation of the impurity and lattice components are demonstrated in the particular case of the isotopes Ga^{69} and Ga^{71}. These effects are based on a version of double nuclear resonance: a quadrupole saturation of the NMR line by an electric field.

An extremely important parameter in rf spectroscopy is the nuclear spin-lattice relaxation time T_1. In real solids, this time is determined by two mechanisms: a lattice mechanism, which is responsible for the relaxation in ideal samples, and an impurity mechanism.[1] The overall spin-lattice relaxation is characterized by a time $T_1^{\Sigma} = \{(T_1^{\text{latt}})^{-1} + (T_1^{\text{imp}})^{-1}\}^{-1}$, whose magnitude, in particular, gives an idea of the impurity structure of the materials of interest. It has not previously been possible to directly separate the times T_1^{latt} and T_1^{imp} in a given sample. The impurity component has been identified only in two ways: (a) by invoking model-based arguments regarding the time dependence, the temperature dependence, or the field dependence of the restoration of the magnetization signal[1–4] or (b) by making a comparison with samples regarded as defect-free. Each of these methods is crude and leaves uncertainties in the separation of T_1^{latt} and T_1^{imp}. In the present letter we describe a new method. Using double resonances, this method is capable of directly measuring the times T_1^{latt} and T_1^{imp} for quadrupole nuclei. The discussion is conducted for the particular case of gallium arsenide crystals.

Impurity nuclear spin-lattice relaxation occurs because relaxation processes are faster by several orders of magnitude near paramagnetic impurities or other defects in a sample than in the main volume. As a result, the local reciprocal spin temperature near a defect, α_{loc}, which is proportional to the local spin magnetization, is closer than the average value over the volume, $\langle\alpha\rangle$, to the equilibrium value, which is equal to the reciprocal of the lattice temperature, α_l: $|\alpha_{\text{loc}} - \alpha_l| < |\langle\alpha\rangle - \alpha_l|$. A local change in spin temperature propagates throughout the volume of the sample by virtue of spin diffusion and thereby affects the rate of change of $\langle\alpha\rangle$. For the most common methods for measuring the spin-lattice relaxation time T_1^{Σ}, based on the recovery of the magnetization signal after saturation, the impurity spin-lattice relaxation evidently proceeds under the condition $\alpha_{\text{loc}} > \langle\alpha\rangle$. If, by means of an additional external perturbation, one can reduce α_{loc} to $\alpha_{\text{loc}} \simeq 0$, i.e., if one can saturate the region near a defect, then one can block the impurity relaxation channel, and the restoration of the average

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magnetization over the volume will be determined exclusively by the lattice mechanism. It will thus become possible to measure T_1^{latt}. As was shown in Refs. 5–7 (GaAs was included in those studies), an effective local heating of the spin system of quadrupole nuclei arises when existing versions of double nuclear resonance (electrical and acoustic saturation of the NMR line) are used, since the probabilities for induced transitions as well as the ratio of these probabilities to the probabilities for relaxation transitions are considerably larger near defects than in the regular lattice. Consequently, if one measures T_1 by the standard method, with a steady-state auxiliary saturation, then one would expect, on the basis of the equations given in Ref. 7, that the impurity relaxation would be turned off beginning at a certain saturation level.[8] Note that the magnetization under saturation conditions is restored with a time scale $\tau = ZT_1$, where Z is a saturation factor, given by $Z = \langle\alpha\rangle_{\text{st}}/\alpha_l$, where $\langle\alpha\rangle_{\text{st}}$ is the value of $\langle\alpha\rangle$ for steady-state electrical or acoustic saturation. This result can be derived without difficulty from the equation for the change in the spin temperature under the influence of steady-state excitation and relaxation.

Figure 1 shows measurements of τ as a function of the factor Z for electrical saturation of the NMR line of Ga^{71} nuclei in high-resistivity GaAs crystals, both nominally pure and doped with Cu^{2+} and Cr^{2+} ions to a concentration of 10^{-3} at.%. These measurements were carried out at 77 K in a magnetic field with an induction

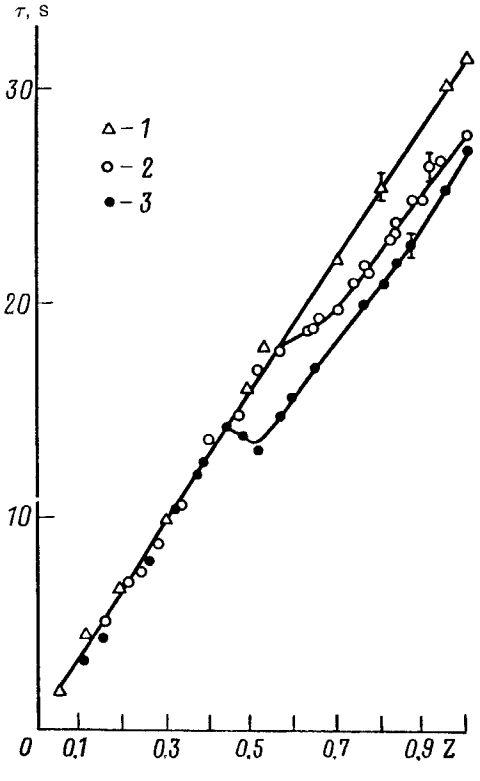

FIG. 1.

$B = 0.42$ T. The saturating electric field was applied at twice the Larmor frequency for the excitation of transitions with a change of 2 in the magnetic quantum number, in the orientation $\mathbf{E}\|[100]\|\mathbf{B}$. From line 1 in Fig. 1 we see that in a pure sample the $\tau(Z)$ dependence is linear: $\tau = T_1^{\Sigma} Z$ with $T_1^{\Sigma} = (31.4 \pm 0.5)$ s. On the basis of the linearity of $\tau(Z)$ and the data on the rate of spin-lattice relaxation,[6] one might suggest that in a pure sample we would have $T_1^{\Sigma} = T_1^{\text{latt}}$ and $T_1^{\text{imp}} \to \infty$. For chromium-doped GaAs with $Z = 1$ we have $T_1^{\Sigma} = (27.8 \pm 0.5)$ s. With decreasing Z, the plot of $\tau(Z)$ becomes a straight line corresponding to an undoped sample (line 2). From the slope of this linear region we can find $T_1^{\text{latt}} = (31.4 \pm 0.8)$ s, which is evidently equal to T_1^{Σ} for pure GaAs. Using T_1^{Σ} and T_1^{latt}, we can calculate $T_1^{\text{imp}} = (240 \pm 40)$ s. For a copper-doped sample (line 3), we find $T_1^{\Sigma} = (27.0 \pm 0.4)$ s and $T_1^{\text{imp}} = 190 \pm 40$ s in a similar way.

Similar $\tau(Z)$ curves were found for the isotope Ga^{69}. From these curves we calculated T_1^{latt} and T_1^{imp}. In a pure sample we found $T_1^{\Sigma} = (12.4 \pm 0.2)$ s $= T_1^{\text{latt}}$; in GaAs:Cr we found $T_1^{\Sigma} = (11.5 \pm 0.2)$ and s $T_1^{\text{imp}} = (160 \pm 50)$ s; and in GaAs:Cu we found $T_1^{\Sigma} = (11.4 \pm 0.2)$ s and $T_1^{\text{imp}} = (140 \pm 50)$ s. We see that the impurity relaxation is relatively less important for Ga^{69} than for Ga^{71}. This conclusion agrees completely with the large quadrupole moment of the isotope Ga^{69}. A similar behavior has been found for other orientations of the vector **E** with respect to the crystallographic axes and the direction of the magnetic field.

In summary, these experiments demonstrate a fundamentally new possibility for directly separating the impurity and lattice components of spin-lattice relaxation. This capability is important in research on the structure of real crystals.

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