NUCLEAR RESONANCE OF Sn^{119} *IN METALLIC TIN*

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The dependence of the second moment of the absorption line of Sn^{119} on the external magnetic field was measured between 900 and 5800 oe in metallic tin. A value of $\delta = 1.0 \times 10^{-3}$ was obtained for the Knight-shift anisotropy. The indirect exchange coupling constant between neighboring nuclei was found to be A = 2.5 kc/sec.

NUCLEAR magnetic resonance in metallic tin was first observed by McGarvey and Gutowsky.[1] They reported that the width of the resonant absorption line was several times greater than what was expected from the dipole-dipole interaction between the nuclei. Later, Bloembergen and Rowland,[2] during an NMR (nuclear magnetic resonance) investigation of tin at high fields, discovered that the line was also strongly asymmetric. They presumed that the anomalous line width and asymmetry could be attributed to anisotropy in the Knight shift of metallic tin.

In fact, finely dispersed samples are always used in NMR experiments on metals, and if the shift is anisotropic an additional source of line broadening exists, associated with the different orientations of the individual crystallites with respect to the external magnetic field. Since the Knight shift is proportional to the external field, its contribution to the line width will increase with increasing field, becoming particularly large in strong fields.

In the present work we investigated the anomalous line width in metallic tin more thoroughly. In order to distinguish between contributions from different causes to the absorption line width, the dependence of the second moment of the absorption line of Sn^{119} on the external field was studied.

An NMR spectrometer described previously[3] was used for the measurements. It is to be noted that in all experiments the instability of the magnetic field and its inhomogeneity over the sample volume, taken together, did not exceed 2×10^{-4} and thus did not contribute to the line width.

All experiments were conducted at the temperature of liquid helium. This yielded a higher signal-to-noise ratio and permitted experiments in small fields.

Measurements were made on two samples, which were prepared by mixing finely powdered metal in vacuum grease and differed in particle size. For one of the samples the powder was obtained by filing tin with a barrette file and contained particles $10 - 30\mu$ in size. This is much greater than the skin depth in tin, which is $2 - 3\mu$ at liquid-helium temperature in the frequency range used.[4] The powdered tin for the other sample was obtained by reducing $SnSO_4$ with fine zinc dust in a 1.5% aqueous solution of gelatin and contained particles $2 - 3\mu$ in size, i.e., of the same order as the skin depth.

As is known, NMR investigation of metals is complicated by the circumstance that the finite depth of penetration of the rf field into the sample causes the resonant absorption to be determined not only by the imaginary part χ'' of the complex nuclear susceptibility $\chi = \chi' - i\chi''$, but also by its real part χ'. This occurs because the value of χ' determines the skin depth: with an increase in χ' the skin depth decreases, and the absorption, other things being equal, decreases. A careful analysis of this problem was made by Chapman, Rodes, and Seymour.[5] In their paper it is shown that the absorption of energy due to nuclear resonance in a finely dispersed metallic sample is determined by the quantity $a\chi' + b\chi''$, where the value of a/b depends on the ratio of the dimension of the particle to the skin depth and approaches unity as the particle size is increased.

It has been observed, however, that the effect of χ' on the absorption line shape is in fact always less than can be expected from this relation.[5,6] Nor did we observe distortion of the absorption lines in our two samples, and their locations and second moments coincided within experimental error.

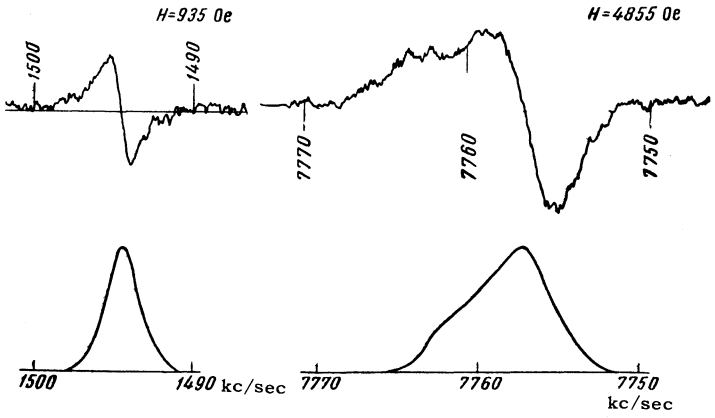

FIG. 1. Upper, derivative traces of Sn^{119} absorption lines; lower, integrated line shapes.

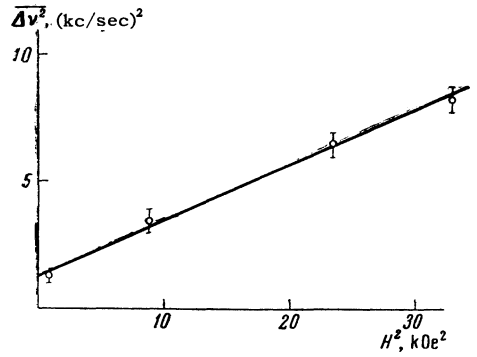

FIG. 2. Dependence of the second moment of the Sn^{119} absorption line on the square of the external magnetic field.

We should like to indicate at this point that there exists at least one effect which will lessen the effect of the real part of the susceptibility on the absorption line shape. Namely, an increase in χ' leads to an increase in the inductance of the resonant circuit in which the sample is located, with the result that the resonant resistance of the circuit increases and with it the amplitude of the rf voltage across the circuit. It is easy to show that when account is taken of this effect the magnitude of the resonance absorption signal is determined by the expression

$$(Q + a/b)\chi'' + (Qa/b - 1)\chi',$$

where Q is the figure of merit of the circuit. Since the Q of a circuit containing much metal is not large, the second term can become significantly less than the first even when the ratio a/b is not very small.

As an illustration, we present in Fig. 1 derivative traces of the absorption lines of Sn^{119} in metallic tin in two different magnetic fields H. It is seen that a marked widening of the line is observed with an increase in field, and asymmetry appears. In Fig. 2 is shown the dependence of the second moment $\overline{\Delta\nu^2}$ on the square of the external field.* This dependence can be expressed in the form

$$\overline{\Delta\nu^2} = kH^2 + \overline{\Delta\nu_0^2}.$$

As already mentioned, the Knight shift is proportional to the external field. Hence the part of the second moment caused by the anisotropy of the Knight shift will be proportional to the square of the field. For tetragonal white tin we can write[7]

$$\overline{\Delta\nu^2}_{\text{anis}} = (1/45\pi^2)\gamma^2\delta^2H^2,$$

where the anisotropy of the Knight shift is

$$\delta = (\nu_{\parallel} - \nu_{\perp})/\nu_0,$$

where γ is the nuclear gyromagnetic ratio, ν_0 the resonant frequency of Sn^{119} in a nonmetallic sample, $\nu_{\parallel}$ and $\nu_{\perp}$ are the resonant frequencies of Sn^{119} in the metal when the field is directed respectively along the tetragonal axis and perpendicular to it.

If one considers that the sole reason for the dependence of the second moment on field is the Knight anisotropy, it is necessary to assume

$$k = (1/45\ \pi^2)\gamma^2\delta^2.$$

From the data presented in Fig. 2 it can then be determined that

$$\delta = (1.0 \pm 0.1)\cdot 10^{-3}.$$

The error indicated here is the scatter of δ in the different experiments.

A value 1.2 ± 0.2 (kc/sec)^2 was obtained for $\overline{\Delta\nu_0^2}$. At the same time, for a sample with natural isotopic composition the second moment caused by dipole-dipole interaction is given by Van Vleck's formula as $\overline{\Delta\nu^2_{\text{dip}}} = 0.15$ (kc/sec)^2, i.e., one-eighth as large.

We can attempt to explain this discrepancy by using the Ruderman and Kittel hypothesis of indirect exchange interaction, between the nuclei in the metal which arises from the conduction electrons. Because of the presence of two different isotopes (Sn^{117} and Sn^{119}), this interaction makes the following contribution to the second moment of the isotope under investigation

$$\overline{\Delta\nu^2_{\text{exch}}} = [I(I+1)/3]f\sum_j A_{ij}^2,$$

where I is the spin, f is the concentration of the other isotope (in our case, Sn^{117}), and A_{ij} is the indirect exchange interaction constant between nucleus i and nucleus j. Assuming $A_{ij} \sim 1/R_{ij}^3$, where R_{ij} is the distance between nucleus i and nucleus j, and summing in $\overline{\Delta\nu^2_{\text{ex}}}$ over the 22 near-

*The second moment was calculated relative to the center of gravity of the line.

est neighbors, we can obtain from our experimental data A = 2.5 kc/sec for the exchange interaction constant between nearest neighbors. This is found to be in qualitative agreement with those values for A which can be derived from Ruderman and Kittel's formula by using reasonable values for the parameters entering into this formula.

In conclusion, we express our deep gratitude fo Academician P. L. Kapitza for his interest in the work, to A. S. Borovik-Romanov for a discussion of the results, and N. N. Mikhaĭlov for assitance in preparing the samples.

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