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HOST NUCLEAR RESONANCE IN Ge : As

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Résumé. — On mesure le temps de relaxation spin-réseau et le déplacement de Knight du noyau ^{73}Ge dans le système Ge : As. La densité du As varie de $7,0 \times 10^{16} \text{ cm}^{-3}$ jusqu'à $1,75 \times 10^{19} \text{ cm}^{-3}$ et les échantillons ne sont pas compensés. La caractérisation des échantillons est obtenue par des mesures de conductivité et d'effet Hall. Les mesures ne révèlent aucun effet des interactions électrons-électrons autour de la transition métal-non métal. Le déplacement de Knight disparaît brusquement à la transition.

Abstract. — Measurements of the spin-lattice relaxation time and of the Knight shift of the ^{73}Ge nucleus in Ge : As are reported. The density range of As is from $7.0 \times 10^{16} \text{ cm}^{-3}$ up to $1.75 \times 10^{19} \text{ cm}^{-3}$ and the samples are uncompensated. The characterization of the samples is supported by conductivity and Hall measurements. There is little or no indication of any electron-electron enhancement of the NMR parameters around the metal-non metal transition. The Knight shift disappears rather abruptly at the transition.

1. Introduction. — The magnetic properties of the impurity band electrons close to the M-I transition have been extensively explored in Si : P using nuclear resonance [1, 2, 3] and electron spin resonance [4, 5, 6] techniques. We present here an interim report on the resonance of the ^{73}Ge nucleus in the related system Ge : As, for twelve samples with a range of doping densities from 7.0×10^{16} to $2 \times 10^{19} \text{ cm}^{-3}$. To be certain of the characteristics of our samples we incorporate some Hall and resistivity measurements for various temperatures.

The Knight shift K results were taken at 5.0 Tesla and the spin-lattice relaxation times T_1 , at 1.44 T. (We are currently working on extending the T_1 measurements to 5.0 Tesla.) All the results were taken using a multi-pulse NMR spectrometer, and the free induction decays were Fourier transformed for the shift measurements.

Section 2 of this paper describes the technical details of sample preparation and the doping densities deduced from Hall and resistivity measurements. Section 3 presents the K and T_1 data, whilst in Section 4 we discuss some of the complications which surround any detailed analysis of these results.

2. Samples. — Germanium samples doped with arsenic were cut from single crystal boules grown by the liquid encapsulated Czochralski technique [7]. The samples were in the form of cylinders ~ 13 mm diameter and ~ 15 mm long with their generating axes perpendicular to the growth axis $\langle 100 \rangle$ of the boule [8]. The two most heavily doped specimens were cut into slices of the order of the skin depth at 7.4 MHz and reassembled with insulating mylar sheets interleaving the germanium slices. Samples [9] 5.9-17 and 5.3-17 were composites formed from

three short cylinders trepanned out of the boule. The composite cylinders were crystallographically marked so that the monocrystalline nature of the total specimens was preserved. Finally, sample 4.4-17 was an irregular shaped composite formed from pieces left after mechanical rupture during fabrication.

The doping densities N_D quoted by the manufacturer were obtained from resistivity and Hall data at 300 K using clover-leaf Van der Pauw samples and a graph of resistivity, ρ_{300} vs. carrier density N_D similar to that of Sze [10]. Our own Hall measurements agree with these derived carrier levels if we assume A at 300 K is unity in the expression [11]

$$N_D = \frac{A}{R_H e} \quad \text{with} \quad A = r \left[\frac{3K(K+2)}{(2K+1)^2} \right]$$

K is the ratio of longitudinal to transverse mass and for conduction band electrons in germanium, the term in brackets is 0.8. The Hall scattering factor r has been shown by Walton and Moss [12] to be greater than unity in our doping density range so that the assumption of $A(300 \text{ K}) = 1$ should not be greatly in error. We note also that the carrier levels derived from the ρ_{300} vs. N_D plot agree well with computed values of the mass fraction of solute (As) dissolved in the boule as a function of distance from seed to tail ⁽¹⁾.

Hall measurements at 4.2 K indicate that the carrier concentration is sensibly independent of temperature for those densities $\geq 3.5 \times 10^{17} \text{ cm}^{-3}$ at room temperature, in agreement with Le Hir [13] and Fritzche [14]. Table I lists the sample characteristics.

⁽¹⁾ JONES, O., RRE, Private communication. We are indebted to O. Jones for helpful communication on these matters.

TABLE I

Sample designation	Carrier density at 300 K ($\times 10^{17} \text{ cm}^{-3}$)	Resistivity at 300 K, ρ_{300} ($\times 10^{-2} \Omega \text{ cm}$)	Resistivity at 4.2 K, $\rho_{4.2} (\Omega \text{ cm})$	Carrier density at 4.2 K ($\times 10^{17} \text{ cm}^{-3}$)
7-16	0.7 ± 0.1	4.35		
2.1-17	2.1 ± 0.2	1.95	1.1	0.72
2.7-17	2.7 ± 0.4	1.62		
2.7-17	2.7 ± 0.3	1.62		
3.1-17	3.1 ± 0.6	1.48	0.12	2.1
3.5-17	3.5 ± 0.5	1.36	0.015	3.5
4.4-17	4.4 ± 0.7	1.16		
5.0-17	5.0 ± 0.25	1.06		
5.3-17	5.3 ± 0.3	1.03		
5.9-17	5.9 ± 0.4	0.96		
9.0-17	9.0 ± 1.5	0.72		
1.75-19	175 ± 55	0.118	0.001 18	175
* K1062b	2.0	1.5	1.2	0.6
* Z184	2.1	1.0	0.062	2.0

(*) From Le Hir, M. J. F. [13].

The low temperature carrier levels were determined from Hall measurements, again assuming, though presumably less appropriately, A equal to unity [5]. We feel, however, that the concentration gradients in our samples are large enough for us to neglect a small variation in A with temperature. These concentration gradients are an inevitable consequence of our requirement of single crystal specimens of the stated dimensions. Our need for large samples was governed by the dictates of signal-to-noise in an NMR experiment.

Finally, we consider the purity of our specimens. The manufacturer quotes background impurity concentrations of $10^{13} \rightarrow 10^{14} \text{ atoms cm}^{-3}$ as deduced from electrical measurements on undoped and low-level doped crystals [7]. Hence, the compensation $\lesssim 0.1\%$. Mass spectrographic data [7] indicate slightly higher contamination but comparison is difficult since nearly all elements searched for are subject to interference from permutations of the five germanium isotopes, multiple charges and single-charged polyatomic species. The deduced compensation ratio is $< 1\%$, however, and we can assume compensation plays no role in our samples.

3. Results. — A summary of the NMR results is presented in figures 1 and 2.

A feature of figure 1 is the simple concentration dependence of the Knight shift, $K \propto N_D^{1/3}$, right down to $N_D = 3.5 \times 10^{17} \text{ cm}^{-3}$. All samples below 3.1×10^{17} show essentially zero shift. Only one sample, $N_D = 3.1 \times 10^{17}$ gives any hint of any intermediate status between the insulating samples

FIG. 1. — Knight Shift K against donor density N_D (in cm^{-3}), taken at 5.0 T and 4.2 K, for the ^{73}Ge nucleus in $\text{Ge}:\text{As}$. The shaded band above the density axis indicates the position of the metal-insulator transition based on the conductivity and Hall measurements. The dashed line is drawn with a slope of $\frac{1}{3}$.

with zero shift and the metallic samples where K lies on the $N_D^{1/3}$ curve.

Figure 2 also demonstrates a very simple concentration dependence; this time though the transition is spanned, with no obvious sharp changes even in the region $N_D = 2$ to $4 \times 10^{17} \text{ cm}^{-3}$. Within experimental error, measurements of the variation with temperature T of T_1 showed that T_1 depends on the inverse of the absolute temperature in all samples with $N_D \geq 3.1 \times 10^{17}$.

If we put together the results shown in figures 1 and 2 to form the Korringa [16] product $K^2 T_1 T$ (bearing in mind that the data in figure 1 were taken

FIG. 2. — T_1 , the ^{73}Ge nuclear spin-lattice relaxation time, measured in minutes, against donor density N_D (in cm^{-3}), taken at 1.44 T and 4.2 K in Ge : As. As in fig. 1 the shaded band above the density axis indicates the position of the metal-insulator transition based on the conductivity and Hall measurements. The dashed line is drawn with a slope of $(-\frac{2}{3})$.

FIG. 3. — The experimental values of the product $K^2 T_1 T$, where T is the absolute temperature, against donor density N_D (in cm^{-3}). The values of K and T_1 are taken from figures 1 and 2. The horizontal line indicates the theoretical value of the product [15], whilst the vertical band above the density axis indicates, as before, the position of the metal-insulator transition.

at a different magnetic field from that in figure 2), then figure 3 is obtained.

4. Discussion. — The proportionality of K to $N_D^{1/3}$ exhibited in figure 1 should be compared to the Si : P data [1, 2]. Our data points correspond well with the data of reference [2], so we must assume that there is some doubt about the measurements on several of the samples in reference [1].

Figure 2, when compared with the Si : P data [1, 2], shows no drop in T_1 below the transition; the amorphous antiferromagnetic system which relaxes the ^{29}Si nuclei strongly in Si : P does not seem to produce

such a marked effect in germanium. At the lower density the dynamics of the coupled electron spin system must be different. The slope of $T_1 : N_D$ throughout the metallic region looks very similar to the Si : P data [2].

The Korringa factors, plotted in figure 3, are all low, except for the highest density sample. This particular sample is very close to the theoretical value of

$$\frac{\hbar}{4\pi k} \frac{\gamma_e^2}{\gamma_n^2}$$

for nuclei relaxed by their Fermi contact hyperfine interaction with an electron gas in which electron-electron effects are negligible. When electron-electron effects are included in the analysis, then the theoretical value of the Korringa product $K^2 T_1 T$ is enhanced [16]. Again, there is some contrast with Si : P results where the measured products are *greater* [2] than the value of

$$\frac{\hbar}{4\pi k} \frac{\gamma_e^2}{\gamma_n^2}$$

The transition to a non-metal in Ge : As occurs at a density an order of magnitude lower than in Si : P; this makes it a very low density electron gas system so that differences in the relative magnitudes of magnetic interactions to bandwidth may be expected in the two systems as the transition is traversed.

A competing relaxation process, in addition to the Fermi contact hyperfine interaction, may account for the low Korringa products in the other metallic samples. The ^{73}Ge nucleus has a quadrupole moment, in contrast to ^{29}Si , so that the reason for the reduction in $K^2 T_1 T$ may just be the presence of a significant quadrupolar mechanism of relaxation, reducing T_1 but not shifting the resonance. Estimates of the size of this effect [17] in germanium show that it should be negligible. However, relaxation by the dipolar interaction [16] of the nuclei with the electron spins is a possibility as an explanation of the anomalously low Korringa products.

Any detailed discussion of these results will have to take into account the problems associated with magnetic freeze-out [18, 19] and the size of the magnetic field relative to both kT and the impurity bandwidths. At 4.2 K and 5.0 T, for instance, $\beta B \sim kT$, and these are the conditions under which the Knight shift data were obtained. The data of Matveev *et al.* [18] show that the increase in the resistance at 5.0 T of a specimen of Ge : As, $N_D = 6.5 \times 10^{17} \text{ cm}^{-3}$, was $\sim 20\%$ of the zero field resistance at 4.2 K.

5. Conclusion. — We have measured nuclear T_1 and K in heavily doped Ge : As; the results confirm the general trend exhibited in Si : P, but do show some differences in detail. In particular the dynamics of the electron spin system just below the metal-

non metal-transition seem to be different, and the exchange enhancement effects are not present immediately above the transition into the metallic region. We confirm the data of Ikehata *et al.* [2], showing that the host Knight shift in these doped semiconductors holds up until immediately above the transition, and that at the transition there is a sharp collapse to zero.

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