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Nuclear Magnetic Resonance in Semiconductors. III. Exchange Broadening in GaAs and InAs

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Nuclear magnetic resonance lines have been observed for the more abundant isotopes of the semiconductors GaAs and InAs. The resonances are broader than expected from nuclear dipolar widths alone. The additional broadening is explained by the indirect nuclear exchange mechanism and is consistent with previous measurements on the homologous semiconductors InSb and GaSb.

INTRODUCTION

NUCLEAR magnetic resonance (NMR) investigations of solids have revealed a variety of interactions between nuclei and their environments. In general, NMR lines in solids are broadened by nuclear dipolar fields. Van Vleck[1] has calculated the dipolar contributions to line widths and numerous experiments have illustrated this effect. Van Vleck's calculation of line widths (actually only second and fourth moments of the absorption are calculated) included the possibility of contributions from exchange fields. Since most of the experiments which followed this study investigated the resonances of light nuclei, hydrogen, and fluorine in particular, it was several years before exchange contributions to the resonance widths were observed. The reason was that the exchange mechanism which has been observed is an indirect exchange process which occurs through the electron-nuclear hyperfine interaction and consequently is more pronounced in the heavier elements. Ruderman and Kittel,[2] in order to interpret Jeffries' observations of the NMR line widths in metallic silver, and Bloembergen and Rowland,[3] independently interpreting their observations on metallic thallium and Tl_2O_3, each postulated the indirect exchange process and derived its consequences. Shortly thereafter an investigation of the semiconductors[4] InSb and GaSb showed the resonances to be broadened considerably by indirect exchange fields.

TABLE I. Line widths and second moments. For InAs and GaAs the values listed in the third column are derived from the experimental results listed in the second column by the relation $\delta H^2 = 4\Delta H_2^2$. For InSb and GaSb, on the other hand, the third column lists measured values of ΔH_2^2. In the last column the differences between the third and fourth columns are listed and attributed to exchange effects.

Nucleus measured	δH (gauss)	ΔH_2^2 (gauss^2)	Calculated $(\Delta H_2^2)_{\text{dipole}}$	$(\Delta H_2^2)_{\text{exch}}$
$Ga^{69}As$	2.43±0.2	1.47	0.79	0.68±0.3
$Ga^{71}As$	2.43±0.2	1.47	0.80	0.67±0.3
$GaAs^{75}$	2.86±0.2	2.04	1.34	0.70±0.3
$In^{115}As$	3.30±0.2	2.72	1.68	1.0 ±0.4
$InAs^{75}$	8.4 ±0.3	17.6 ±2	3.60	14.0 ±2
$Ga^{69}Sb$	5.1 ±0.15	6.5 ±0.4	1.20	5.3 ±0.4
$Ga^{71}Sb$	5.6 ±0.15	6.2 ±0.4	1.20	5.0 ±0.4
$GaSb^{121}$	4.7 ±0.2	6.7 ±0.4	1.05	5.6 ±0.4
$GaSb^{123}$	5.1 ±0.2	8.4 ±1	0.93	7.4 ±1
$In^{115}Sb$	9.0 ±0.2	24 ±1	1.65	22 ±1
$InSb^{121}$	17.5 ±1	65 ±4	2.52	62 ±4

We can consider the indirect electron exchange to arise from a hyperfine interaction between electron and nucleus. As a result the electronic state is perturbed to accommodate a polarization of the electronic spins. The electronic polarization is conveyed to a nearby nucleus by the hyperfine interaction and in this manner the fields at one nucleus are influenced by the dipole orientations of another. With heavy atoms, where the hyperfine interactions are strong, the exchange fields will exceed the dipole fields. Since the strength of the interaction involves a virtual excitation of the electron to higher energy states it is, to a degree, a measure of the excited states. In order to extend the measurements previously reported on GaSb and InSb, NMR measurements were made on the more abundant isotopes of the homologous compounds GaAs and InAs.

EXPERIMENTAL

Measurements were made either with a Varian Associates Variable Frequency Induction spectrometer or with a modified Pound-Knight-Watkins[5,6] spectrometer. Magnetic field sweep was used and the absorption derivative recorded. Suitable precautions were taken to prevent modulation broadening and saturation. In the GaAs sample the Ga^{69}, Ga^{71}, and As^{75} resonances were observed and in InAs we measured In^{115} and As^{75}. Both samples were polycrystalline and were powdered to allow uniform penetration of the radio-frequency fields. Both the GaAs and InAs were *n* type with $\sim 10^{17}$ carriers/cc. The separations between derivative extrema, called δH, were measured and are listed in the second column of Table I along with similar data on InSb and GaSb reported previously. Line shapes in GaAs were determined to be Gaussian by fitting them to Gaussian shape functions. The stronger $In^{115}As$ resonance was not Gaussian because of the presence of

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[1] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[2] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

[3] N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

[4] Shulman, Mays, and McCall, Phys. Rev. **100**, 692 (1955).

[5] R. V. Pound and W. D. Knight, Rev. Sci. Instr. **21**, 219 (1950).

[6] Mays, Moore, and Shulman (to be published).

symmetrical wings that caused it to fall off slower than a Gaussian line. For Gaussian lines the line width δH is related to the second moment by the expression $\delta H^2 = 4\Delta H_2^2$. We have neglected departures from Gaussian shapes and have converted the widths into second moments which are listed in the third column of Table I. Dipole contributions to ΔH_2^2 have been calculated from Van Vleck's formula and are presented in the fourth column. The differences between ΔH_2^2 and $(\Delta H_2^2)_{\text{dipole}}$ are listed in the last column.

INTERPRETATION

Several factors make it apparent that only semiquantitive agreement between the data and the indirect nuclear exchange theory can be expected in these compounds. The assumption of Gaussian line shapes in InAs (which are predicted by the exchange broadening mechanism) is not well justified by the experiments as mentioned in the previous section. We have arbitrarily assumed that δH is a measure of the Gaussian width and that the additional broadening in the wings does not affect this value appreciably. Another experimental limitation is that the differences between dipolar widths and measured widths are much smaller than in the antimonides, in fact only barely outside of experimental error. This means that the relative contributions of exchange broadening to different resonances will be difficult to confirm. However the magnitude of the exchange broadening is well established by the measurements.

The theory of indirect exchange interactions has been extended to semiconductors by Anderson.[4,7] By using this theory to fit the experiments we would obtain some information about the excited states of InAs and GaAs. However, because of the experimental limitations, it is not felt that any information obtained about the energy surfaces would be trustworthy. Therefore we have decided to use the "empty lattice" approximation for the energy bands which was found to be applicable to the antimonides. In this way we determine the applicability of exchange broadening to the NMR lines while at the same time we eschew obtaining any additional information about the energy bands.

Exchange contributions to the second moment of the ith nuclei are

$$\langle \Delta\nu_i^2 \rangle_{\text{Av}} = \tfrac{1}{3} \textstyle\sum_f [I_f(I_f+1) \textstyle\sum_j A_{ij}^2(R_{ij})], \tag{1}$$

where subscripts f refer to different nuclear species and $A_{ij}(R_{ij})$ is the exchange interaction with the jth nucleus of type f which may be a function of distance R_{ij}. Anderson[7] has shown for semiconductors that, to a first approximation,

$$A_{ij}(R_{ij}) = \frac{3.36\times 10^{-7}\Omega^2 m^* \xi_i \xi_j \psi_i^2(0)\psi_j^2(0)\mu_i\mu_j}{I_i I_j R_{ij}^4}\ \text{sec}^{-1}, \tag{2}$$

where Ω = atomic volume,

$$m^* = 4(m_e^* m_h^*)^{\frac{3}{2}}(m_e^* + m_h^*)^{-2},$$

m_e^* and m_h^* are effective masses for electrons and holes, respectively, $\psi_i^2(0)$ = the probability of finding the outer s electron of atom i at its nucleus, and

$$\xi_i = \frac{[\psi_i^*(0)_{\text{hole}}\psi_i(0)_{\text{electron}}]_{\text{solid}}}{[\psi_i^2(0)]_{\text{atom}}}.$$

Additional details of the interaction have been discussed previously[4,7] and will not be repeated here.

In the appropriate "empty lattice" approximation the electron and hole are assumed to have the free-electron mass and a wave function characteristic of the free-atom functions that merge to form the band. Each electron and hole in these compounds, therefore, has one-quarter s character and the mass of the free electron. This means that $\xi_i\psi_i^2(0)$ and $\xi_j\psi_j^2(0)$ are the undetermined parameters in Eq. (2). If we make the reasonable assumption that $\xi_{\text{Ga}}\psi_{\text{Ga}}^2(0)$ is the same in GaAs and GaSb, then we can calculate the relative values of $\xi_{\text{As}}\psi_{\text{As}}^2(0)$ and $\xi_{\text{Sb}}\psi_{\text{Sb}}^2(0)$ in these two compounds. By making the same assumption about indium in InSb and InAs, it is possible to determine the same ratio of density functions in this pair of compounds.

Substituting in Eq. (1), we find the ratios of the second moments to be

$$\frac{\Delta H_2^2(\text{Ga}^{69}\text{Sb})}{\Delta H_2^2(\text{Ga}^{69}\text{As})} = \frac{[(\%\ \text{Sb}^{121})(I_{121})(I_{121}+1)A_{69-121}^2 + (\%\ \text{Sb}^{123})(I_{123})(I_{123}+1)A_{69-123}^2]}{[(I_{75})(I_{75}+1)A_{69-75}^2]}. \tag{3}$$

Substituting further and bearing in mind that atomic volumes are proportional to the lattice constants cubed, we find numerically

$$\frac{\Delta H_2^2(\text{Ga}^{69}\text{Sb})}{\Delta H_2^2(\text{Ga}^{69}\text{As})} = 4.2\frac{\xi_{\text{Sb}}^2\psi_{\text{Sb}}^4(0)}{\xi_{\text{As}}^2\psi_{\text{As}}^4(0)} = \frac{5.0(\text{gauss})^2}{0.67(\text{gauss})^2}. \tag{4}$$

If we assume that $\xi_{\text{Sb}} = \xi_{\text{As}}$ then we find that $\psi_{\text{Sb}}^2(0)/\psi_{\text{As}}^2(0) = 1.3$, while if we follow the same procedure in analyzing the In^{115}As data with respect to In^{115}Sb we find this ratio to be 2.3. The average of these is 1.8 which, considering the experimental accuracy, is in agreement with the factor of ~two predicted by the Fermi-Segrè[8] formula for these two atoms.

In conclusion we can say that the NMR lines in InAs and GaAs are broadened by indirect exchange effects and that the magnitude of this broadening is consistent with the exchange broadening previously studied in InSb and GaSb.

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[7] P. W. Anderson, Phys. Rev. **99**, 623 (1955) and private communication.

[8] E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933).