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Density of the Conduction Electrons at the Nuclei in Indium Antimonide

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The Overhauser shift of the electron spin resonance due to the natural nuclear polarization at liquid-helium temperatures has been used to measure the conduction-electron density at the nuclei in *n*-type InSb. The results are: $|\psi(R_{\mathrm{In}})|^2=(9.35\pm1)\times10^{25}$ cm^{-3}, and $|\psi(R_{\mathrm{Sb}})|^2/|\psi(R_{\mathrm{In}})|^2=1.70\pm0.1$ indicating that the electron is equally shared between the In and Sb ions. This is discussed in relation to the chemical bond and effective charge. Hot-electron effects in relation to nuclear polarization and the Overhauser effect are presented.

INTRODUCTION

THERE have been several magnetic resonance studies on the semiconductor InSb. Nuclear coupling by indirect exchange,[1] electrical field gradients caused by impurities,[2] or external stress[3] have been studied by nuclear resonance, as well as relaxation by quadrupolar interactions.[4] Following magneto-optical studies,[5] the absolute value of the electronic g factor ($g^*\approx-50$) and its variation with the Fermi level in the conduction band were measured by electron spin resonance[6] (ESR); the sign of g^* given by theory was confirmed by a study of the Overhauser shift of the ESR[7,8] and, later, by other experiments which also ascribed a partial electrical-dipole character to the spin transition.[9] A nuclear polarization was achieved by electrical heating of the kinetic energy of the electrons in a high magnetic field[10] and a study by ESR of the heating in low magnetic field has been reported.[11]

InSb is well suited for Overhauser-shift experiments, because of the strong hyperfine interaction, due to the high atomic numbers of the atoms involved; the narrow electron spin resonance can be shifted appreciably by the *natural* polarization of the nuclei in a 10-kG field at liquid-helium temperatures.

In the present experiments we have determined the electron densities $|\psi(R_{\mathrm{In}})|^2$ and $|\psi(R_{\mathrm{Sb}})|^2$ for the bottom of the conduction band, at the In and Sb nuclei, by the Overhauser shift. The field in which ESR is observed is chosen high enough (500 G) for thermal mixing between different nuclear-spin species to be very small during the measurements. We have compared our values of $|\psi(R)|^2$ with those for the free atoms and tried to relate the data to estimations based on current conceptions of the chemical bond in this compound.

An enhanced nuclear polarization would have been helpful for the measure of the $|\psi(R)|^2$. Using a dc electric field, the polarization by hot electrons, first observed by Clark and Feher,[10] has been obtained. However, this polarization is not homogeneous in our sample, which makes it unsuitable for the electron-density measurements. The electrons have also been heated by a *microwave* electric field; as with a dc field, the polarization is inhomogeneous. The microwave heating will be discussed in relation to polarization of the nuclei by the Overhauser effect.[12]

1. THE HYPERFINE INTERACTION

The hyperfine interaction in the case where the g factor of the conduction electrons is large has been calculated by Yafet.[13] The large effective magnetic moment $g^*\beta$ can be attributed to orbital currents spread over regions larger than the unit cell, which couple to an average value of the magnetic field. In the same way, they couple to an average value of the magnetic field due to the nuclear moment, giving to the hyperfine interaction a contribution of the order of $g^*\beta(1/\Omega)\mu_n$. On the other hand, the usual atomic type contribution, in which the contact interaction dominates, will be of the order of $g\beta|\psi(R)|^2\mu_n$, where g has the free-electron value.

Here β is the Bohr magneton, μ_n the nuclear moment, Ω the volume of the unit cell containing one In and one Sb ion, and $|\psi(R)|^2$ the electron density on the nucleus at site R normalized in the volume Ω.

In the case of InSb, the wave function of the electrons, at the bottom of the conduction band, is mainly s-like. With $\Omega=0.68\times10^{-22}$ cm^3 (Ref. 14), $|\psi(R)|^2\approx10^{26}$ cm^{-3} (Ref. 1) and $g^*\approx-50$ we get for the ratio of orbital to contact interaction:

$$\left|\frac{g^*}{g}\frac{1}{\Omega|\psi(R)|^2}\right|\approx4\times10^{-3}.$$

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The contact interaction is thus dominant; in the following, no other contribution will be retained.

2. THE OVERHAUSER SHIFT

The electron spin Hamiltonian is

$$\hbar\mathcal{H}=g^*\beta\mathbf{S}\cdot\mathbf{H}+\frac{8\pi}{3}g\beta\sum_i|\psi(R_i)|^2\langle\boldsymbol{\mu}_i\rangle\cdot\mathbf{S}$$

$$=g^*\beta\mathbf{S}\cdot\left(\mathbf{H}+\frac{8\pi}{3}\frac{g}{g^*}\sum_i|\psi(R_i)|^2\langle\boldsymbol{\mu}_i\rangle\right).$$

Due to the magnetization of the nuclear species i, the electron thus "sees" a magnetic field:

$$\mathbf{h}_i=(8\pi/3)(g/g^*)\psi(R_i)|^2\langle\boldsymbol{\mu}_i\rangle, \quad (1)$$

where $\langle\boldsymbol{\mu}_i\rangle=\hbar c_i\gamma_i\langle\mathbf{I}_i\rangle$ is the mean magnetic moment of nuclear species i in the unit cell; c_i is the isotopic abundance, γ_i the gyromagnetic ratio, $\langle\mathbf{I}_i\rangle$ the mean value of the nuclear spin[15] (Table I).

A given $\langle\mu_{iz}\rangle$ along the direction of the magnetic field H (z axis) will thus give a shift h_{iz} (Overhauser shift) of the conduction-electron spin resonance.

The destruction of $\langle\mu_{iz}\rangle$ (by saturation of the nuclear resonance) will produce a shift-h_{iz} from which the value of $|\psi(R_i)|^2$ can be evaluated. The determination of the $|\psi(R_i)|^2$ is possible only if one can saturate separately the different nuclear resonances in the magnetic field H_0 corresponding to the ESR. With $g^*\approx-50$, H_0 is 130 G for the 3-cm band, 500 G for the 8-mm band, and it is not evident that the different nuclear-spin temperatures that occur when the resonance of one species only is saturated can be maintained during a time long enough to carry out the measure of the shift corresponding to the saturated species. It is shown in the Appendix that thermal mixing at 130 G is too fast to allow the measurement of the $|\psi(R_i)|^2$ but that no difficulty is encountered at 500 G, and this is the reason for operating at this field.

A possible systematic error must be mentioned: the nuclei of Sb and In have appreciable quadrupolar moments, and quadrupolar broadening due to crystal imperfections might be expected. In an imperfect region of the sample, irradiation at one nuclear resonance frequency would then not saturate all the spins of the species, but only those that would happen to be in states $m_z=\pm\frac{1}{2}$, the transition $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ being unperturbed by the first-order quadrupolar interaction; because of the partial and inhomogeneous saturation, a reduced Overhauser shift and a broadening of the esr would be observed. Rhoderick[2] has measured the absolute intensity of the nuclear resonance of In^{115} in monocrystalline undoped InSb, and found it equal to 0.8±0.1 of the calculated value, indicating some quadrupolar effects. However, these may be unimportant in our experiments, for two reasons. First, those nuclei whose energy levels are quadrupolarly displaced will be in strained regions of the crystal; these regions probably contribute little to the ESR which, as we have observed, is very sensitive to strains; second, the quadrupolarly shifted satellites may be spread far enough from the center of the line to be unobservable but yet near enough to be in thermal contact with the unperturbed nuclei.

TABLE I. Nuclear constants and second moments of the resonance lines.

Nucleus	Isotopic abundance%	Spin	Gyromagnetic ratio γ	$(\Delta\omega^2)^{1/2}$ (rad/sec)
In^{115}	95.84	$\frac{9}{2}$	$+5.86\times10^3$	29×10^3
In^{113}	4.16	$\frac{9}{2}$	$+5.84\times10^3$	
Sb^{121}	57.25	$\frac{5}{2}$	$+6.40\times10^3$	51×10^3
Sb^{123}	42.75	$\frac{7}{2}$	$+3.47\times10^3$	28×10^3

3. MEASUREMENT OF THE OVERHAUSER SHIFT

Our sample is a n-type single crystal ($n=2\times10^{14}$ cm^{-3}) isolated from a polycrystalline ingot obtained from Ohio Semiconductors. Its size is 2×3×0.2 mm. It exhibits an ESR line for which $g^*=-50.7$ at 4.2°K. In a field $H_0=500$ G, its width (peak to peak of the derivative) is 1.8 G.

The nuclear relaxation times have been measured on a large (0.8 cm^3) coarsely powdered sample taken from the same ingot. The hypothesis of relaxation due to fixed paramagnetic impurities and spin diffusion[16] through the indirect interaction gives a magnetic field dependence and a value for $T_1(\mathrm{Sb}^{123})/T_1(\mathrm{Sb}^{121})$ in good agreement with experiment.[17]

The observation technique is the same as in Ref. 8. After polarizing the nuclei in a high magnetic field (9320 G), the field is brought to the ESR value (500 G). While observing the ESR we destroy the magnetization of one nuclear species by irradiation at its Larmor frequency. The resulting shift of the ESR then determines $|\psi(R)|^2$ [formula (1)]. The shifts are 0.1 G in order of magnitude, and can be measured with a precision of a few percent. The necessary sensitivity is achieved by the use of a superheterodyne esr spectrometer and lock-in detection.

The sample lies on the end wall of a rectangular TE 104 cavity, slit to permit the penetration of the nuclear-resonance saturating radio frequency produced by an external coil.

Absolute Value of $|\psi(R_{\mathrm{In}})|^2$

The temperature of the experiment is 4.2°K. We first polarize the nuclei during 24 h in a high magnetic field

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[15] Formula (1) can also be written: $\mathbf{h}_i=(g/g^*)(8\pi/3)|\psi(R_i)|^2\Omega\times\langle\boldsymbol{\mu}_i\rangle1/\Omega$. The dimensionless number $|\psi(R_i)|^2\Omega$ is equal to $|\psi(R_i)|^2/\langle|\psi|^2\rangle$ and $\langle\boldsymbol{\mu}_i\rangle/\Omega$ is the magnetization (magnetic moment per unit volume).

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[17] M. Guéron, Thesis, Paris, 1964 (unpublished).

(9320 G) for which the T_1 of the In spins is 4.2 h. The magnetization thus differs by a negligible amount from the thermal equilibrium value, and the effect of errors in the measure of T_1 becomes small. The field is then brought to the ESR value of 500 G in which $T_1=1.3$ h. While the measurement is being prepared, two minutes elapse during which the polarization decreases by 2%. To measure the Overhauser shift-h_{In} created by saturation of the In resonance,[18] we balance it by sending a direct current in the modulation coils, previously calibrated with a proton-resonance probe.

From our three best measurements, we extract for the value of h_{In} corresponding to thermal equilibrium at $T=4.2$°K, in a field $H=9320$ G:

$$h_{\mathrm{In}}=-156\pm15\mathrm{mG}.$$

Introducing the value of $\langle\mu_{\mathrm{In}}\rangle=\gamma^2\hbar^2 I(I+1)H/3kT=5.06\times10^{-27}$ cgs and the value $g^*=-50.7$, Eq. (1) gives:

$$|\psi(R_{\mathrm{In}})|^2=(9.35\pm1)\times10^{25}\ \mathrm{cm}^{-3} \qquad (2)$$

or $|\psi(R_{\mathrm{In}})|^2\Omega=6350$.

Ratio of $|\psi(R_{\mathrm{Sb}})|^2$ to $|\psi(R_{\mathrm{In}})|^2$

We could in principle determine $|\psi(R_{\mathrm{Sb}})|^2$ by the same method as $|\psi(R_{\mathrm{In}})|^2$; however, the relaxation times in high field are uncomfortably long: ≈10 h for Sb^{121}, even more for Sb^{123}; a more convenient method can be used, which also has the advantage of giving directly the ratio $h_{\mathrm{Sb}}/h_{\mathrm{In}}$ from which we shall deduce the value of $r=|\psi(R_{\mathrm{Sb}})|^2/|\psi(R_{\mathrm{In}})|^2$, a significant parameter in the discussion of the results.

In this experiment, after polarizing the nuclei in a high field and before measuring the shifts, we establish a common spin temperature among all spins by thermal mixing in a low field (50 G). The magnetizations are then accurately proportional to $c_i\gamma_i^2 I_i(I_i+1)$, where c_i is the isotopic concentration. A check for the mixing in low field is afforded by the ratio of the shifts relative to Sb^{121} and Sb^{123} (Fig. 1).

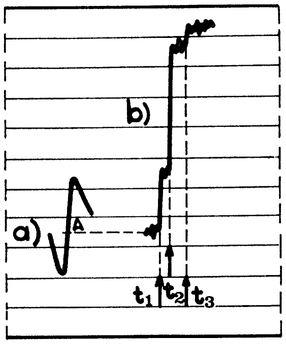

FIG. 1. (a) Derivative of the spin resonance of the conduction electrons. $H=500$ G. (b) The field is set at the value corresponding to point A, close to the middle of the line. At times t_1, t_2, t_3, an rf field at Larmor frequency destroys the magnetizations of Sb^{121}, In, Sb^{123}, respectively. The shifts of the resonance line change the level at the recorder. The gain is ten times larger than in (a).

No absolute values come in this measurement. It is therefore possible to let the temperature vary during the polarization of the nuclei (between 4.2 and 1.5°K) and also to accelerate the polarization of Sb^{121} and Sb^{123} by mixing their spins in a low field with those of In, every 2 h for instance. Polarizations corresponding for all species to a spin temperature of 4°K are then obtained after only 5 h.

The relative shifts can be measured directly on the recordings. From the three best experiments, we get:

$$h_{\mathrm{Sb}^{121}}/h_{\mathrm{In}}=0.41\pm0.02.$$

From Eq. (1), we have:

$$r=\frac{[c\gamma^2 I(I+1)]_{\mathrm{In}}}{[c\gamma^2 I(I+1)]_{\mathrm{Sb}^{121}}}\,\frac{h_{\mathrm{Sb}^{121}}}{h_{\mathrm{In}}}=4.14\frac{h_{\mathrm{Sb}^{121}}}{h_{\mathrm{In}}}.$$

This gives

$$r=1.70\pm0.1, \qquad (3)$$

a value somewhat higher than that deduced by Clark and Feher from their hot-electron experiments: $r=1.35\pm0.1$.

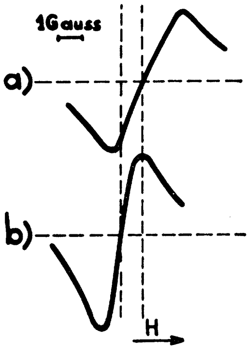

FIG. 2. Derivative of the spin resonance of the conduction electrons. (a) The nuclei have been polarized by "heating" of the kinetic energy of the electrons, by an electric field, in a high magnetic field; the inhomogeneous nuclear magnetization shifts and broadens the esr. (b) After destruction of the nuclear magnetizations, the line recovers its initial place and width.

4. HOT-ELECTRON EFFECTS

In InSb, small electric fields can heat the kinetic-energy distribution of the conduction electrons appreciably. In high magnetic fields the nuclei are thereby polarized.[10]

We have considered the possibility of using the enhanced nuclear magnetization to increase the precision of the $|\psi(R)|^2$ measurements. The enhancements were measured by the Overhauser shifts and were of 5 to 10 for In with dc electric fields of ≈1 V/cm.

However the nuclear polarization resulted not only in an Overhauser shift but also in a broadening of the esr. The broadening disappeared after destruction of the nuclear polarizations and is attributed to a distribution of the Overhauser shifts, reflecting directly the inhomogeneity of the nuclear polarization (Fig. 2).

The change of shape of the ESR on destruction of the nuclear polarizations made it impossible to use this method for a precise measure of the Overhauser shift.

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[18] The gyromagnetic ratio of the little-abundant isotope In^{113} is very close to that of In^{115} (Table I) and the two resonance lines overlap even in high fields. In the following, we shall always consider In^{113} and In^{115} as one spin species, denoted In.

We have also heated the electrons by a microwave electric field. The sample is placed on the bottom of the cavity, exactly as for the observation of the ESR. The microwave source is precisely that used for ESR. The heating is monitored by the variation of the ESR g factor as a function of microwave power. When the kinetic energy of the electrons is heated, the ESR is instantaneously shifted (as with a dc electric field[11]) because of the variation of g^* with the wave vector k in the nonparabolic conduction band (Fig. 3). A detailed study of this effect will be published later.

When the heating takes place in a high magnetic field, a nuclear polarization is obtained, inhomogeneous, as with a dc field.

The electric fields arise in connection with the eddy currents produced by the microwave magnetic field in a sample of thickness comparable to the spin depth ($\delta=2\times10^{-2}$ cm at 36 kMc/sec). With a resistivity of $\approx 1\ \Omega$-cm, a magnetic field of one tenth of a gauss may be shown to generate an electric field of approx 1 V/cm, corresponding to the absorption of 1 mW in a 10^{-3} cm^3 sample.

Although the electric field is inhomogeneous, the fact that the esr is not much broadened upon heating (Fig. 3) shows that the temperature of the electrons does not vary much over the sample; this can be explained by the diffusion of the electrons.

Lastly, it should be noted that unless extremely small samples are used, the (nonresonant) heating of the kinetic energy by the microwave electric field will overcome the (resonant) saturation of the spins by the microwave magnetic field. Enhancement of the nuclear polarization by an Overhauser effect will then be hindered; this may explain why attempts to observe this effect have up to now been unsuccessful.

5. DISCUSSION OF THE RESULTS

At the minimum of the conduction band, located at $k=0$, the wave function has s symmetry under the rotations of the tetrahedral group. Lacking theoretical estimates, we approximate it by a linear combination of atomic functions $\phi_{5s\mathrm{In}}$, $\phi_{5s\mathrm{Sb}}$ centered on the corresponding nuclei in the unit cell:

$$\psi=A[\alpha\phi_{5s\mathrm{In}}-(1-\alpha^2)^{1/2}\phi_{5s\mathrm{Sb}}]. \tag{4}$$

The coefficient A, whose value is close to 1, normalizes ψ in the unit cell; α^2 and $1-\alpha^2$ could be considered to express the distribution of the electron between the two ions.

The value of the atomic wave function centered on a given nucleus being much higher, at the site of that nucleus, than the values of functions centered on other nuclei, we get:

$$r=\frac{1-\alpha^2}{\alpha^2}\,\frac{|\phi(0)|^2{}_{5s\mathrm{Sb}}}{|\phi(0)|^2{}_{5s\mathrm{In}}}. \tag{5}$$

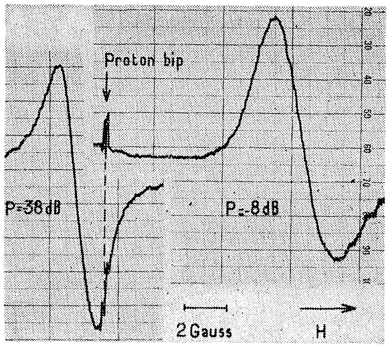

FIG. 3. Heating of the kinetic energy of the electrons by the microwave electric field associated with the microwave magnetic field at the ESR frequency. The microwave power is 1 μW at left, 1 mW at right. The displacement corresponds to a kinetic temperature of 20°K ($f=36$ kMc/sec, $T=1.5$°K).

By Ref. 1,

$$|\phi(0)|^2{}_{5s\mathrm{Sb}}=24\times10^{25}\ \mathrm{cm}^{-3}, \tag{6}$$
$$|\phi(0)|^2{}_{5s\mathrm{In}}=16\times10^{25}\ \mathrm{cm}^{-3}.$$

From relations (2)–(6), we get

$$\alpha^2=0.47 \quad \text{and} \quad A^2=1.25. \tag{7}$$

The value of α^2, *close to 0.5, indicates that the electron is distributed nearly equally on the In and Sb ions.*

Relation to the Chemical Bond

We do not know of a theoretical estimation of the wave function at the bottom of the conduction band in InSb. Such an estimation would necessitate a good description of the valence electrons, which is not available. We shall recall the notion of an effective charge e^*, and its relation to the chemical bond. Next, we present experimental determinations of the effective charge which suggest that the chemical bond is not far from neutral. Lastly we discuss our results in relation to the neutral bond.

(a) The atomic configurations being $5s^25p$ for In and $5s^25p^3$ for Sb, there are eight electrons in the valence band per unit cell containing one In and one Sb ion. The states of the valence band are built from atomic $5s$ and $5p$ orbitals of In and Sb.

The contributions of the In and Sb orbitals to the wave function of a given state of the valence band will result in a certain spatial distribution of the electron between In and Sb. Summing this distribution over the states of the valence band, and subtracting the charges of the ion cores, one then obtains the total charge e^* (effective static charge) on the ions.

The effective charge can be used to characterize the chemical bond. If the bond is supposed "covalent" with configurations $\mathrm{In}^{-}5s^25p^2$, $\mathrm{Sb}^{+}5s^25p^2$, the effective charge is $e^*=-1$. If the bond is supposed "ionic" (In^{3+}, $\mathrm{Sb}^{3-}5s^25p^6$), then $e^*=+3$. Slater and Coster[19] suggest that the bond is close to "neutral" ($\mathrm{In}^{0}5s^25p$, $\mathrm{Sb}^{0}5s^25p^3$), with $e^*=0$, in all the III-V semiconductors.

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[19] J. C. Slater and G. F. Coster, Phys. Rev. **94**, 1499 (1954).

(b) Effective charge values can be measured by various methods. However, the interpretation of the results is a matter of discussion and the concept of an effective charge itself is not perfectly well defined. For instance, the effective charge derived from the infrared lattice reflection may depend strongly on the polarization induced by the vibration of the ions. The effective charge can also be derived from the static spatial-charge-density distribution, measured by x-ray techniques; the value of e^* will then depend on the choice of the ionic volumes, because the electron density does not vanish between the ions.

The infrared data provide only the absolute value of the effective charge. From recent experiments,[20] using a formula due to Szigeti,[21] a value of 0.42 is obtained, indicating a bond rather close to the neutral bond. This is in agreement with current ideas on this compound. However, it has been suggested[22] that the Szigeti formula is not valid in the III-V compounds; a modified interpretation of the infrared data is proposed, yielding an absolute value of 2.7 for the effective electric charge.

The x-ray data[23] indicate that $e^* = -0.45$, that is, there are 3.45 electrons on In, and 4.55 on Sb. These measurements, the only ones which give the sign of e^*, thus suggest a bond intermediate between the covalent and neutral.

(c) From the preceding data a bond close to neutral seems a reasonable assumption, although the matter is not settled.

In the Slater and Coster[19] picture of the neutral bond the states of the valence band are built from bonding orbitals, the In and Sb functions contributing in the ratio of 3 to 5 (neutral bond); as for the states of the conduction band, they are built from antibonding orbitals constructed from the same atomic $5s$ and $5p$ functions so that the In and Sb functions this time contribute in the inverted ratio of 5 to 3.

If the contributions of In and Sb when going from the bottom of the valence band to the top of the conduction band change from 3:5 to 5:3 in a progressive way, it seems reasonable that these contributions be approximately equal at the bottom of the conduction band, as we have inferred from the Overhauser shifts. One can also remark that if the bond is neutral, the periodic potential seen by the conduction electron will be small outside the ion cores, so that again an equal distribution could be suggested.

Our results would therefore seem to favor a bond close to neutral. However, detailed calculations will be necessary before more affirmative statements can be made. Starting with a model of the valence band, it should be possible to calculate the $|\psi(R)|^2$; comparison with the experimental values could then shed light on the validity of the model, and thus on the chemical structure of InSb.

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APPENDIX: THERMAL MIXING BETWEEN THE NUCLEAR SPINS

Couplings (dipolar, indirect exchange$\cdots$) between different nuclear spins may induce thermal mixing by mutual flips when resonance frequencies and linewidths are such that energy can be conserved in the process. The thermal mixing therefore depends strongly on the overlap of the resonance lines, and consequently on magnetic field, line shapes, and linewidths.[24–26]

Thermal mixing is possible between In and Sb^{121} by a mutual spin flip because the resonance lines overlap. For Sb^{123}, whose resonance frequency is close to one-half that of Sb^{121}, the principal mixing mechanism is that of simultaneous flips of two Sb^{123} and one Sb^{121}, as for F^{19} and Li^7 in lithium fluoride.[25]

Theoretical Estimation of Mixing Times

A formal expression for the mixing time is given by Provotorov.[26] Its numerical evaluation would however be quite burdensome, and we will therefore use approximate formulas discussed in Ref. 25.

The thermal mixing time between Sb^{123} and Sb^{121} would be given by:

$$\frac{1}{\tau}=\frac{1}{T_2}\frac{\Delta^2\omega_{\mathrm{Sb}^{123}}}{\omega^2{}_{\mathrm{Sb}^{123}}}\exp\left[-\frac{1}{2}\frac{(\omega_{\mathrm{Sb}^{121}}-2\omega_{\mathrm{Sb}^{123}})^2}{\delta^2{}_{\mathrm{Sb}^{121}}+2\delta^2{}_{\mathrm{Sb}^{123}}}\right], \qquad \text{(A1)}$$

and that between In and Sb^{121} by:

$$\frac{1}{\tau'}=\frac{1}{T_2}\exp\left[-\frac{1}{2}\frac{(\omega_{\mathrm{In}}-\omega_{\mathrm{Sb}^{121}})^2}{\delta^2{}_{\mathrm{In}}+\delta^2{}_{\mathrm{Sb}^{121}}}\right]. \qquad \text{(A2)}$$

In these expressions, T_2 is a typical inverse linewidth.

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[26] B. N. Provotorov, Zh. Eksperim. i Teor. Fiz. **42**, 882 (1962) [English transl.: Soviet Phys.—JETP **15**, 611 (1962)].

TABLE II. Mixing times between Sb^{121} and $Sb^{123}(\tau)$ and between In and $Sb^{121}(\tau')$ from Eqs. (A1) and (A2). The first figure is calculated with $\delta^2=\Delta\omega^2$, the second with $\delta^2=0.7\Delta\omega^2$.

H_0(gauss)	τ(sec)		τ'(sec)	
130	0.5	0.7	2×10^{-3}	3×10^{-3}
500	10^5	5×10^6	36	3500

The δ^2 are of the order of the second moments $\Delta\omega^2$ of the resonance lines, (Table I) but could be smaller by 25 to 50%.[25] The dipolar and pseudodipolar contributions to the coupling between spins make them anisotropic.

The main defect in (A1) and (A2) is the lack of precision in the estimate of δ^2, resulting in a large possible error in $1/\tau$, $1/\tau'$. On the other hand, these formulas indicate the main features of the mixing: very strong dependence on magnetic field and linewidth.

The values for τ and τ', calculated from (A1) and (A2), are shown in Table II. Two values are given, corresponding, respectively, to $\delta^2=\Delta\omega^2$ and $\delta^2=0.7\Delta\omega^2$.

They suggest that the measure of the separate shifts will be impossible at 130 G. They show that at 500 G, the shift of Sb^{123} can be measured with no hindrance due to mixing (however, this shift is rather small), and that there is a chance that mixing may not prohibit separate observation of the In and Sb^{121} shifts.

Study by the Overhauser Shift

The experiments at 130 G in the 3-cm band have been reported in Ref. 8. After the nuclei had been polarized in a high field, the ESR was observed. The same Overhauser shift was produced by irradiation at any one of the three resonance frequencies of In, Sb^{121}, Sb^{123}; subsequent irradiation at the same frequency or at another of the three resonance frequencies failed to shift the line further, indicating that the different nuclear-spin systems had all been saturated. (When irradiating at the Sb^{123} frequency, a filter was used to eliminate the possibility of a distortion generated second harmonic saturating the Sb^{121} line directly.)

The rf field could easily be made strong enough to saturate the corresponding nuclear resonance in a time short compared to the time resolution of our cw microwave spectrograph (approx 0.3 sec). The shift was then always completed in a time no longer than this. This shows that in the 130-G field, thermal mixing between the three spin systems is achieved in a time smaller than 0.3 sec. This is not in conflict with the theoretical estimates.

In the 500-G field, the mixing times are longer. Because our principal interest was in the measure of the $|\psi(R)|^2$ and not in the thermal mixing, we have not made a thorough study of the latter. In a first experiment, we observed that there is no very fast mixing: Successive saturation of the three nuclear resonances results in three successive shifts of the ESR (Fig. 1).

In a second experiment, after polarizing the nuclei, we saturate Sb^{121}. This creates an immediate shift. We now keep the rf field on, so that the temperature of the Sb^{121} spins stays infinite. The In nuclei are then heated by thermal mixing, and the corresponding shift should set in with the time constant of the mixing.

This turns out to be so long that spin-lattice relaxation is appreciable during the experiment ($T_{1\mathrm{In}}=1.3$ h). We estimate that τ' is of the order of 45 min; this fits in the enormous bracket of Table II.

No measure has been attempted of the mixing times of Sb^{123} with In or with Sb^{121}. We are content with the observation that these times are not short (see above) and with the theoretical estimate which indicates that they are extremely long.

Lastly, it should be made clear that the measure of the $|\psi(R)|^2$ at 500 G is carried out in such a way that the results would in any case be only little affected by thermal mixing. The shift of In is measured after polarizing the nuclei for 24 h; this is longer than the rerelaxation times of In and Sb^{121} in the polarizing field, so that the spin temperatures of the two species are not very different. One calculates that mixing would tend in this case to establish a temperature differing from the initial temperature of In by only 3%.

For the measure of the relative shifts of In and Sb^{121}, the two systems are at first at a common temperature, and therefore insensitive to mixing; and because only 10 sec separate the saturations of the two systems in this experiment, no appreciable mixing can occur during this interval.

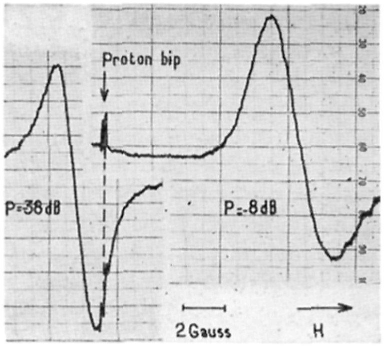

FIG. 3. Heating of the kinetic energy of the electrons by the microwave electric field associated with the microwave magnetic field at the ESR frequency. The microwave power is 1 μW at left, 1 mW at right. The displacement corresponds to a kinetic temperature of 20°K ($f=36$ kMc/sec, $T=1.5$°K).