It also is possible to estimate A_1 as does Morse[7] in a semiempirical fashion from the known elastic scattering cross section σ_t, noting that in the same approximation as Eq. (40) the elastic scattering amplitude is $2f_a(\theta)j_0(\frac{1}{2}kr_0)$. With $\sigma_t=4.8\pi a_0^2$ we obtain $f_a(\theta)=0.55a_0$, which, substituted in Eq. (44), implies A_1/A_2 is about 0.05 at 0.6 ev in N_2. Hence this method of estimating A_1 indicates it is in fact negligibly small even at 0.6 ev; in any event it supports the view that Eq. (46) is not a gross underestimate of A_1/A_2.

Finally, we mention some other "near-field" effects which, like A_1, depend on details of the short-range interaction and are decreasingly important as the incident energy approaches zero. These effects include: (1) distortion of the wave function by a very large $ef_2(r)P_2(\mathbf{r},\mathbf{s})$ interaction, such as was inferred (Fig. 4) from the parameters of Duncanson and Coulson,[31] thereby possibly modifying the estimate from Eq. (36) of the ratio of the second to first Born approximation; (2) the contribution, appearing in second Born approximation, which the short-range spherically symmetric $f_0(r)$ term of Eq. (37) makes to the inelastic amplitude A_{ab}; (3) electron exchange, which plays no role in the "far field," where the incident and atomic electron wave functions do not overlap. To sum it up, our approximations are of such a character that for any homonuclear gas, not merely N_2, the cross sections of Eq. (20) are increasingly reliable as the incident electron energy decreases to zero, because with diminishing energy the long-range tail of the interaction becomes increasingly important.

ACKNOWLEDGMENTS

We wish to express our thanks to Dr. T. M. Donahue for his comments and advice. We have greatly profited from discussions with Dr. A. V. Phelps, who suggested the problem to us. We are especially indebted to Dr. T. Holstein for a number of very important and illuminating suggestions.

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Nuclear Spin Exchange in Solids: Tl^{203} and Tl^{205} Magnetic Resonance in Thallium and Thallic Oxide*

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The line width of the Tl^{203} and Tl^{205} nuclear magnetic resonance in thallium and thallium oxide greatly exceeds the dipolar width, and is a function of the abundance of the other isotope. The results can be interpreted in terms of an exchange interaction $A\mathbf{I}_1\cdot\mathbf{I}_2$ between a pair of nuclear spins which exceeds the normal dipolar interaction. The exchange between different isotopes leads to broadening. Exchange between like nuclei should lead to narrowing, but it was found that samples containing 98.7 percent Tl^{205} still exhibit lines broader than the dipolar interaction. Two causes are shown to exist: anisotropy of the chemical shift and pseudo-dipolar exchange interaction. Analysis with the method of the moments gives for the exchange interaction constant $Ah^{-1}=17.5$ kc/sec with a 30 percent anisotropic pseudo-dipolar character in the hexagonal metal, and $Ah^{-1}=12$ kc/sec with less than 10 percent pseudo-dipolar character in thallic oxide. The oxide has a chemical shift of +0.55 percent with an anisotropy of 34 percent of this amount. The metal exhibits a shift of 1.56 percent with 16 percent anisotropy.

Ramsey's theory of the nuclear spin exchange via excited electron states in molecules, is extended to solids. Most heavy isotopes in metals and insulators should exhibit exchange effects. From the anisotropy of the exchange, information about the relative amount of p or d character of the electron wave function in the solid can be obtained.

It is predicted that thallic oxide has a nuclear Curie point at 3.5×10^{-6} °K. Whether it will become nuclear ferromagnetic or antiferromagnetic depends on details of the electronic band structure.

I. INTRODUCTION

In an earlier paper[1] an anomalous behavior of the Tl^{203} and Tl^{205} magnetic resonance lines in metallic thallium had been noted, but no satisfactory explanation was given at that time. It was found that the width of the Tl^{205} resonance was about 10 times as large as could be expected from the dipolar broadening, but even more anomalous was the fact that the Tl^{203} resonance was again much broader than the Tl^{205} resonance. The two isotopes both have a spin $I=\frac{1}{2}$, and the magnetic moment of Tl^{203} is only one percent smaller than that of Tl^{205}. Quadrupolar effects are thus excluded. The only reason why the two isotopes could behave differently seemed to be contained in the fact that they occur in unequal abundance. Natural thallium contains 29.5 percent Tl^{203} and 70.5 percent Tl^{205}. Consequently a Tl^{203} nucleus has fewer identical neighbors than a Tl^{205} nucleus. The dipolar width of the Tl^{203} resonance should therefore be smaller than that of Tl^{205}. An exchange interaction of the type $A_{12}\mathbf{I}_1\cdot\mathbf{I}_2$ between the nuclear spins would act in the opposite direction.

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* This research was supported by the Office of Naval Research.

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[1] N. Bloembergen and T. J. Rowland, Acta Metallurgica 1, 731 (1953).

Whereas the exchange between like spins causes exchange narrowing, the exchange between unlike isotopic species would cause broadening. The effect of like and unlike magnetic ingredients with dipolar and exchange interaction on the width of magnetic resonance lines has been discussed extensively by Van Vleck.[2] If the exchange interaction between two thallium nuclei were ten times as large as the classical dipolar interaction, the observations in natural thallium could be explained.

This required magnitude at first sight appears improbably large. The exchange type of coupling between nuclear spins in molecules is well known both experimentally[3,4] and theoretically.[5] It occurs via the intermediate excitation of electron orbits. Clearly similar effects could be expected in solids. The order of magnitude of exchange interaction is $A=(W_{\text{hfs}})^2/\Delta E$ where W_{hfs} is the hyperfine interaction in the molecule or solid and ΔE is an appropriate average distance of the excited electronic state from the ground state.

In all observed molecular spectra the exchange coupling is only a small fraction of the dipolar coupling. In the HD-molecule, e.g., the exchange is 43 cps, whereas the dipolar interaction is more than a hundred times as large. In the molecule undergoing frequent collisions in the liquid or the gas, the dipolar interaction averages out to zero making the exchange effect observable. In a rigid lattice of light elements the exchange effect would be completely obscured by the dipolar interaction. All observations on molecules have been done on light isotopes, mostly H, D, F^{19} and P^{31}. The exchange interaction could be much larger for heavier compounds. The hyperfine interaction in atomic thallium is, e.g., twenty times larger than for hydrogen. If one makes the crude assumption, that the hyperfine interaction in metallic thallium is also twenty times as large as in the hydrogen molecule and that the "average excited state"—the meaning of this expression will be made more precise later in this paper—is the same for thallium and the hydrogen molecule, an exchange interaction of 17 kc/sec is obtained between a neighboring pair of thallium nuclei in the metallic lattice. This would have the right order of magnitude to explain the experimental observations. It might be expected that in most compounds with predominantly heavy isotopes the exchange effects will outweigh the classical dipolar interaction.

In order to test the hypothesis of a large exchange interaction, experiments have been carried out on a series of thallium samples with different isotopic compositions, as the effect of exchange interaction is markedly different between like and unlike pairs. These experimental results are described in Sec. II. The phenomenological theory is described in Sec. III and the experimental results are interpreted in terms of this theory in Sec. IV. It proved necessary to introduce a tensor-type exchange, or pseudo-dipolar, interaction in addition to the scalar interaction. Furthermore evidence for the anisotropy of the chemical shift in thallium oxide is presented. This type of anisotropy has not been reported before in the literature.

In the remaining sections an atomistic interpretation of the phenomenological exchange constants introduced in Sec. III is presented. It is an extension of Ramsey's theory[5] for molecules to the periodic lattice. The interaction is a kind of superexchange via intermediate excited electronic states. A second-order perturbation calculation in the electron-spin-nuclear-spin interaction is required.

While this research neared completion, Ruderman and Kittel independently put forward the hypothesis of nuclear spin exchange in metals via the intermediary of the conduction electrons.[6] Their theory was developed along the same lines mentioned above. We extend their method to include the case of insulators and the pseudo-dipolar interaction. The latter is especially important in pure or nearly pure isotopes and gives valuable information about the angular dependence of the wave function in the solid. An interesting feature of nuclear spin exchange is that theoretical expressions for its magnitude can be given. A detailed study of the theoretically simpler nuclear exchange may serve to elucidate problems in magnetism related to electron spin exchange.

II. EXPERIMENTAL RESULTS

The equipment was the same as used in the earlier investigation.[1] A permanent magnet provided a field of 5560 oersted in a $1\frac{1}{4}$ inch gap. Field values were always corrected for temperature variations (−1.0 oersted/degree). Experiments at a lower field of 3288 oersteds were carried out with an electronically current-regulated electromagnet. The pole faces were 5 inches in diameter and the inhomogeneity across the sample was always less than 0.2 oersted. It never contributed significantly to the width of the observed broad lines. The field was modulated at 280 cps and the nuclear absorption was detected with a radio-frequency spectrometer of the Pound-Knight-Watkins type.[7] The output of the 280-cps "lock-in" detector, which represents the derivative of the absorption curve, was recorded on an Esterline-Angus recording instrument. For the detection of the weak lines the time constant of the lock-in was made as long as 30 seconds. The scanning rate was usually about 2 kc/min, and it might take as long as 90 minutes to go completely through a

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

[3] E. L. Hahn and D. E. Maxwell, Phys. Rev. 88, 1070 (1952).

[4] Gutowsky, McCall, and Slichter, J. Chem. Phys. 21, 279 (1953).

[5] N. F. Ramsey, Phys. Rev. 91, 303 (1953); N. F. Ramsey and E. M. Purcell, Phys. Rev. 85, 143 (1953).

[6] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954). We are indebted to Prof. Kittel for making this manuscript available before publication.

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

resonance line. To obtain a more favorable signal-to-noise ratio all data were taken at 77°K. A few checks on the temperature dependence of the lines were made between 77°K and 300°K. No dependence of the line breadth on temperature was found.

The samples consisted of finely powdered metallic thallium and thallic oxide. The metal particles had a diameter small compared to the skin depth and were suspended in paraffin oil. The metal and the oxide of natural abundance were obtained commercially (cp grade). Enriched isotopic samples of Tl_2O_3 were obtained from the AEC stable isotope division, which also provided the mass and spectrographic analysis listed in Table I.

The impurity content is low enough not to affect the breadth or shape of the resonance. The amount of paramagnetic impurity was high enough to provide a conveniently short relaxation time in the oxide, avoiding saturation effects. The relaxation time in the metal is determined by the interaction with the conduction electrons. It may be estimated with the Korringa relation[8] from the observed relaxation time $T_1 = 2\times10^{-3}$ sec in copper[9] at 300°K, and the known Knight shifts of 0.23 percent for copper[10] and 1.56 percent for thallium. One finds $T_1 = 10^{-5}$ sec in thallium at 300°K, and 3.9×10^{-5} sec at 77°K. The contribution to the width $\Delta\omega/2\pi$ from the finite relaxation time is therefore about 4 kc/sec at 77°K. This agrees qualitatively with the absence of any temperature effect on the observed line widths in the metal, which are always larger than 16 kc/sec. Experimentally the effects of T_1 are negligible. It may well be that the Korringa relation gives too small a value for T_1 in thallium.

After data on the enriched oxide samples had been taken, they were reduced by holding at 260°C in a slow stream of pure hydrogen gas. Complete reduction was established by weighing and the metal was obtained in the form of a fine powder, directly suitable for the nuclear resonance experiment. This procedure had first been tested by the reduction of oxide of the natural composition.

Data were taken on all samples, the oxide and the metal with five different isotopic compositions, each at two external field strengths, $H_{\text{ext}} = 5560$ and 3288 oersteds, respectively. Both the Tl^{203} and the Tl^{205} were recorded. These isotopes have nearly the same gyromagnetic ratio[11] $g_{205}/g_{203} = 1.009838$, and $g_{205} = 2\pi\nu_{\text{res}}/H_{\text{res}} = 1.546\times10^4$ sec^{-1} oersted^{-1}. This last value is determined on the assumption that in a concentrated aqueous solution of thallium acetate $H_{\text{res}} = H_{\text{ext}}$. In other words, this value is not corrected for diamagnetism of the core or a small chemical shift of less than two parts in ten thousand, which may exist in the solution and depends on the concentration of the acetate ions.[11] It was found that the resonance field in the oxide was 0.55 percent higher than the external field. This indicates a chemical shift of +0.55 percent in this solid. The metal exhibits a Knight shift of 1.56 percent.

TABLE I. Composition of enriched thallium samples.

Abundance of Tl^{205} (percent)	Quantity of element in grams	Dominant impurities (percent)
98.7±0.5	0.1014	Si: 0.08
90.5±0.5	1.7005	Mn: 0.04
70.5	commercial	Pb: 0.01 Fe <0.001
52.1±0.5	0.3230	V <0.04
14.0±0.5	0.4161	Fe <0.04 Mn <0.02 Si <0.08

Typical recordings are reproduced in Fig. 1 for the oxide in the higher field. It is seen at a glance that the hypothesis of a large exchange interaction is correct. The Tl^{205} line becomes narrower, the smaller the Tl^{203} concentration, and the Tl^{203} line becomes narrower, the smaller the Tl^{205} concentration. For the 48 percent Tl^{203}–52 percent Tl^{205} composition the lines are nearly identical, as each isotope has the same average number of nonequivalent neighbors.

The resonance in 98.7 percent pure Tl^{205} is of special interest. One would expect a line narrower than the dipolar width due to exchange narrowing between like neighbors. The observed resonance is still several times broader than the dipolar width and exhibits a marked asymmetry. A similar type of asymmetry had been noted previously in powdered tetragonal tin and was interpreted as an anisotropy of Knight shift. The hypothesis that the asymmetric line in the powdered $(Tl^{205})_2O_3$ is due to an asymmetry in the chemical shift is confirmed by the recordings at lower field. Whereas the dipolar and exchange broadening are independent of H_0 and the width of the Tl^{205} resonance in samples with a relatively high Tl^{203} concentration is field independent, the width of the 98.7 percent Tl^{205} resonance is much smaller at the lower field and the asymmetry is markedly reduced. The integrated absorption curves obtained from the experimental recordings are shown in Fig. 2. The crystal structure of Tl_2O_3 is cubic,[12] but anisotropy is possible as the individual thallium nuclei are not in positions of cubic symmetry. The unit cell contains thirty-two thallium atoms. Eight of these are located on the body diagonals of the unit cell and therefore have threefold axial symmetry. They have six nearest neighbors at 3.35 A, and six others at 3.95 A. The other twenty-four thallium atoms are in position of low symmetry. They have four neighbors at 3.35 A,

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[8] J. Korringa, Physica **16**, 601 (1950).

[9] A. E. Redfield (to be published).

[10] Townes, Herring, and Knight, Phys. Rev. **77**, 852 (1950).

[11] H. S. Gotowski and B. R. McGarvey, Phys. Rev. **91**, 81 (1953).

[12] R. W. G. Wyckoff, *Structure of Crystals* (Interscience Publications, New York, 1931), p. 253.

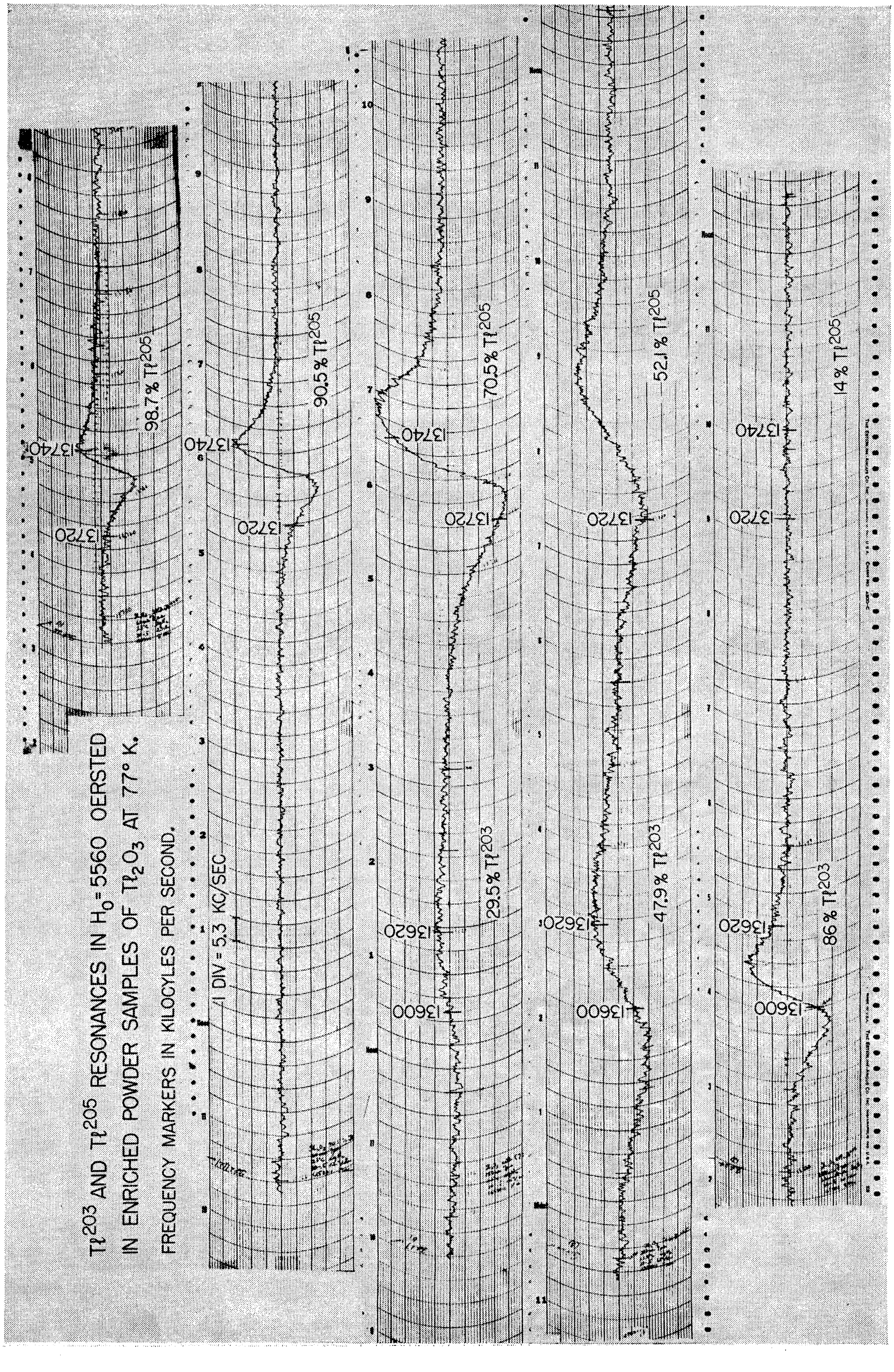

Fig. 1. Experimental recordings of the derivative of the nuclear magnetic resonance absorption in Tl_2O_3 for various isotopic compositions.

two at 3.48 A, four at 3.75 A, and two at 3.95 A. Other neighbors are relatively much farther away.

Experimentally the distance between the maximum and minimum in the derivative curve is most accurately determined. This width between points of maximum slope, $\Delta\nu_{msl}$, is unfortunately not accessible to direct theoretical interpretation. The second moment of the line,

$$\langle\Delta\nu^2\rangle_{\text{Av}}=\int\nu^2 f(\nu)d\nu,\quad \int f(\nu)d\nu=1,$$

has more theoretical significance, but especially the contribution from the tails of experimental curves is rather hard to evaluate with precision. The method of evaluation has been described by Pake and Purcell.[13] Table II lists the values of $\Delta\nu_{msl}$ and $[\langle\Delta\nu^2\rangle_{\text{Av}}]^{\frac{1}{2}}$, determined as an average over several recordings. The ratio in the last column of Table II should be 2.0 for a pure Gaussian and 0 for a Lorentzian type of curve. If an effective second moment for the Lorentzian is identified with the square of the half-width at half-maximum absorption, the ratio would be 1.15. It is seen that qualitatively the character of the line shape changes from Gaussian to Lorentzian, as the abundance of the unlike species is reduced. Of course, the table does not give an indication of the asymmetry discussed previously.

TABLE II. Line width of nuclear magnetic resonance in Tl_2O_3 in 77°K.

		Tl^{205} resonance		
Percent abundance Tl^{205}	H_{ext} in oersted	$\Delta\nu_{msl}$ kc/sec	$[\langle\Delta\nu^2\rangle_{\text{Av}}]^{\frac{1}{2}}$ kc/sec	$\frac{\Delta\nu_{msl}}{[\langle\Delta\nu^2\rangle_{\text{Av}}]^{\frac{1}{2}}}$
98.7	5560	8.3	8.4	1.
90.5	5560	10.5	9.5	1.1
70.5	5560	20.	14.	1.4
52.1	5560	32.	17.	1.9
14.0	5560	>60.	>20.	3.
98.7	3288	5.6	5.9	
90.5	3288	7.4	7.5	
70.5	3288	18.0	14.0	
Percent abundance Tl^{203}		Tl^{203} rsonance		
29.5	5560	48	19	2.5
47.9	5560	33	17.5	1.9
86.0	5560	14	11	1.3
86.0	3288	11	10	

Data for the 52 percent–48 percent composition at low fields are not listed. In this case the Tl^{203} and Tl^{205} resonances are not entirely separated, as the exchange interaction becomes comparable to the energy difference between the unperturbed Tl^{203} and Tl^{205} resonance. The integrated derivative curve gives the absorption line shown in Fig. 3. It should be noted that as the two resonances begin to coalesce, the resonance maxima pull inward from their unperturbed positions. The distance between the maxima is reduced by 21 percent in this case.

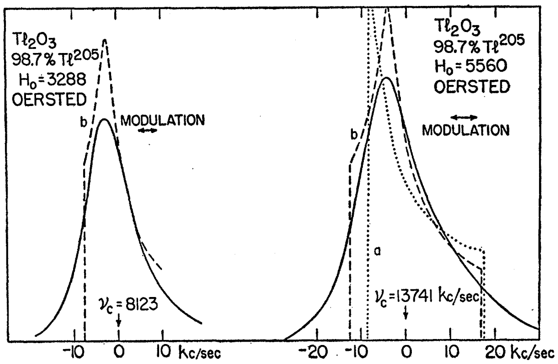

FIG. 2. Integrated line shapes of the Tl^{205} resonance in Tl_2O_3 with 98.7 percent Tl^{205} at two different field strengths. The dotted curve (a) is the theoretical shape for powders with axial symmetry and (b) for lower symmetry. 25 percent of curve (a)+75 percent of curve (b) with the addition of a small amount of dipolar broadening should be compared with the full-drawn experimental curve.

Turning to the corresponding results in the metal, it may be remarked at the outset that these are qualitatively similar to those in the oxide, although there are important quantitative differences. The data in Table III were collected from a set of recordings which are not reproduced, but are similar to those for the oxide shown in Fig. 1.

The lines are broader than in the corresponding oxide samples, indicating a larger exchange interaction. The lines again change gradually from approximately Gaussian to Lorentzian character as the unlike isotope concentration decreases. Again the case of 98.7 percent pure Tl^{205} is of special interest. No pronounced exchange narrowing is observed. On the contrary, the line is about seven times as broad as the dipolar interaction

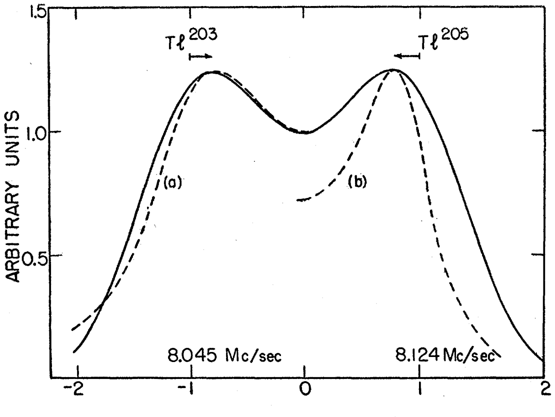

FIG. 3. The Tl^{203} and Tl^{205} resonance in Tl_2O_3 in a low magnetic field. The integrated experimental line shape is given by the full-drawn curve. The two resonances have shifted from the unperturbed positions at ±1 on the horizontal axis and begin to merge. Dotted curves (a) and (b) are two theoretical shapes, represented by Eqs. (23) and (25), respectively.

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[13] G. E. Pake and E. M. Purcell, Phys. Rev. 74, 1184 (1948).

TABLE III. Line width of nuclear magnetic resonance in metallic thallium at 77°K.

		Tl^{205} resonance		
Percent abundance Tl^{205}	H_{ext} in oersted	$\Delta\nu_{msl}$ kc/sec	$[\langle\Delta\nu^2\rangle_{\text{Av}}]^{\frac{1}{2}}$ kc/sec	$\frac{\Delta\nu_{msl}}{[\langle\Delta\nu^2\rangle_{\text{Av}}]^{\frac{1}{2}}}$
98.7	5560	20	17	1.2
90.5	5560	23	20	1.2
70.5	5560	33	24.2	1.4
52.1	5560	54	28.5	1.9
14.0	5560	>60	33	>2
98.7	3288	16.7	15	1.1
90.5	3288	19	16.8	1.1
70.5	3288	33	24.2	1.4
Percent abundance Tl^{203}		Tl^{203} resonance		
70.5	5560	>60		
52.1	5560	54		
14.0	5560	27		
14.0	3288	25		

for the nearly pure isotope would lead to predict. This time, however, the width is not much dependent on the field strength and the asymmetry is not pronounced. This is shown clearly by the experimental derivative curves, reproduced in Fig. 4. Perhaps the slight asymmetry in the higher field and the small field dependence could be attributed to the anisotropy of Knight shift in the hexagonal metal. Each thallium atom has six neighbors at 3.401 A and six neighbors at 3.450 A in the almost ideally close-packed structure. The major cause for the line broadening, however, must be found elsewhere. It will be interpreted in terms of a pseudo-dipolar or tensor-exchange interaction.

The lines in the lower field in thallium of natural abundance begin to overlap appreciably but even the 30 percent Tl^{203} line is observable. In the 50 percent–50 percent composition, however, no resonance was observed. Apparently the exchange interaction has the same magnitude as the unperturbed splitting. The process of which the onset was shown in Fig. 3 for the oxide, is so advanced in the metal, that an extremely broad unobservable structure results. The interesting effects which may occur at still lower fields will be discussed in the next section. A complete merger of the two lines may be expected for fields less than 10^3 oersteds. One trial run in the metal of natural abundance at $H=1600$ oersteds has been made. It would be necessary to cool to liquid helium temperatures to determine the structure with any precision.

This qualitative description of the experimental results has shown what factors should be considered in the theory of magnetic line broadening in these powdered thallium and thallium oxide samples. They are: ordinary dipolar interaction, pseudo-dipolar interaction and nuclear spin exchange between like and unlike pairs of nuclear spins, and anisotropy of the chemical or Knight shift. The influence of the finite spin-lattice relaxation time can be neglected.

III. PHENOMENOLOGICAL THEORY OF LINE BROADENING AND LINE SHAPE

(a) Second Moment Calculation

The basis for a quantitative interpretation of the results is Van Vleck's theory[2] of magnetic resonance line broadening. The Hamiltonian for a system with two magnetic ingredients is, in Van Vleck's notation,

$$\mathcal{H}=\mathcal{H}_z+\mathcal{H}_{\text{ex}}+\mathcal{H}_{\text{dip}}, \tag{1}$$

$$\mathcal{H}_z=g\beta H\sum_j I_{zj}+g'\beta H\sum_{k'} I_{zk'}, \tag{1a}$$

$$\mathcal{H}_{\text{exch}}=\sum_{i>j}\tilde{A}_{ij}\mathbf{I}_i\cdot\mathbf{I}_j+\sum_{k'>l'}\tilde{A}_{k'l'}\mathbf{I}_{k'}\cdot\mathbf{I}_{l'}+\sum_{jk'}\tilde{A}_{jk'}\mathbf{I}_j\cdot\mathbf{I}_{k'}, \tag{1b}$$

$$\begin{aligned}\mathcal{H}_{\text{dip}}=&\sum_{i>j}(g^2\beta^2r_{ij}^{-3}+\tilde{B}_{ij})[\mathbf{I}_i\cdot\mathbf{I}_j-3r_{ij}^{-2}(\mathbf{I}_i\cdot\mathbf{r}_{ij})(\mathbf{I}_j\cdot\mathbf{r}_{ij})]\\&+\sum_{jk'}(gg'\beta^2r_{jk'}^{-3}+\tilde{B}_{jk'})[\mathbf{I}_j\cdot\mathbf{I}_{k'}-3r_{jk'}^{-2}\\&\times(\mathbf{I}_j\cdot\mathbf{r}_{jk'})(\mathbf{I}_{k'}\cdot\mathbf{r}_{jk'})]+\sum_{k'>l'}(g'^2\beta^2r_{k'l'}^{-3}+\tilde{B}_{k'l'})\\&\times[\mathbf{I}_{k'}\cdot\mathbf{I}_{l'}-3r_{k'l'}^{-2}(\mathbf{I}_{k'}\cdot\mathbf{r}_{k'l'})(\mathbf{I}_{l'}\cdot\mathbf{r}_{k'l'})].\end{aligned}$$

In our case the unprimed symbols may refer to Tl^{205} and the primed symbols to Tl^{203}. $\mathcal{H}_z$ is the Zeeman energy in the magnetic field H. The exchange and dipolar interactions are separated into pairs of primed and unprimed variety alone, and into mixed pairs. The $\tilde{B}$'s represent the pseudo-dipolar interaction. The mean square absorption frequency of the unprimed resonance is given by

$$h^2\langle\nu^2\rangle_{\text{Av}}=g^2\beta^2H^2+\tfrac{1}{3}I(I+1)\sum_j B_{ij}^2+\tfrac{1}{3}I'(I'+1)\sum_{k'} C_{ik'}^2, \tag{2}$$

$$B_{ij}=-\tfrac{3}{2}(\tilde{B}_{ij}+g^2\beta^2r_{ij}^{-3})(3\cos^2\theta_{ij}-1), \tag{2a}$$

$$C_{ik'}=\tilde{A}_{ik'}-(\tilde{B}_{ik'}+gg'\beta^2r_{ik'}^{-3})(3\cos^2\theta_{ik'}-1), \tag{2b}$$

where θ_i is the angle between $\mathbf{r}$ and $\mathbf{H}$. The exchange interaction between equivalent spins does not contribute to the second moment. Certain simplifying assumptions will now be made to bring (2) into a form which will permit direct comparison with the experimental results.

In the powders the contribution of each spin pair has to be averaged over all angles θ. Using

$$\langle 3\cos^2\theta-1\rangle_{\text{Av}}=0,\quad \langle(3\cos^2\theta-1)^2\rangle_{\text{Av}}=\tfrac{4}{5},$$

it is seen that the exchange and the dipolar interaction between unlike spins contribute independently to the second moment. This result would still be approximately true in many single crystals when each spherical shell contains a sizeable number of atoms.

In powders the effective field H may depend on the

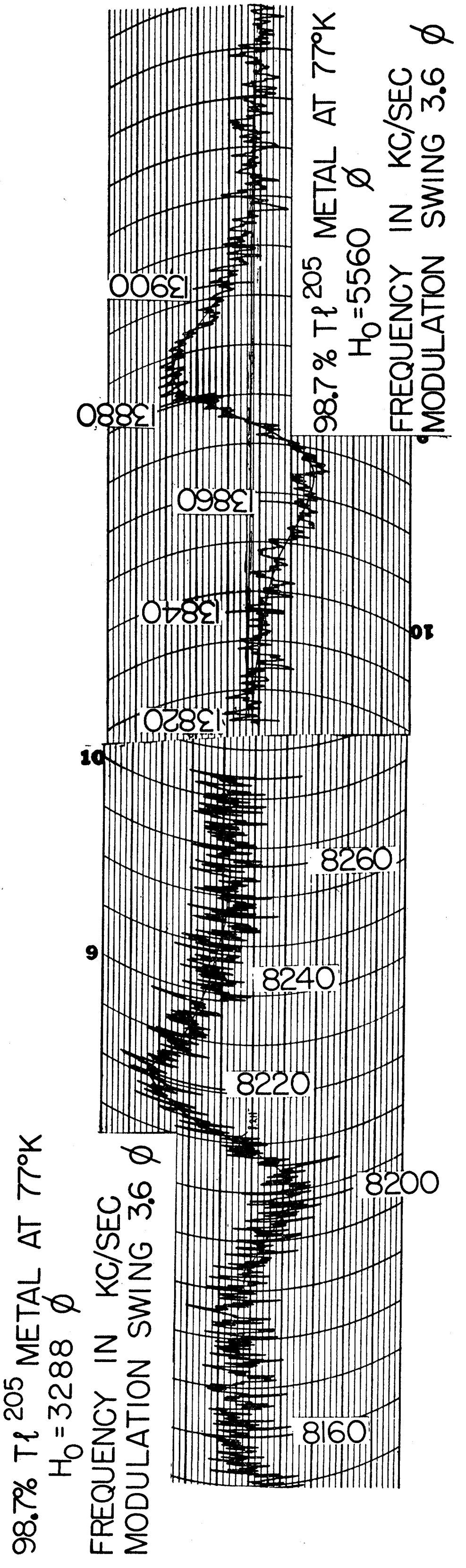

Fig. 4. Experimental recordings of the derivative of the nuclear magnetic resonance absorption in 98.7 percent Tl^{205} metallic thallium at two different field strengths.

orientation of the crystallite,

$$\mathbf{H}=(\mathbf{1}^d+\boldsymbol{\delta}^d)\cdot\mathbf{H}_{\mathrm{ext}},$$

where $\mathbf{1}^d$ is the unit dyadic and $\boldsymbol{\delta}^d$ is the chemical shift tensor, which has a fixed relation to the crystallographic axes. Since $|\boldsymbol{\delta}|\ll 1$, the omission of terms quadratic in $|\boldsymbol{\delta}|$ leads to

$$|H|=|H_{\mathrm{ext}}|\{1+\delta_{\mathrm{is}}+\delta_{\mathrm{ax}}(3\cos^2\theta-1)+\delta_{\mathrm{asym}}\sin^2\theta\cos 2\phi\},\quad(3)$$

where θ and ϕ specify the orientation of H with respect to the chemical shift ellipsoid. The chemical shifts in the three principal directions are

$$\begin{aligned}(\nu_1-\nu_0)\nu_0^{-1}&=\Delta\nu_1/\nu_0=\delta_{\mathrm{is}}+2\delta_{\mathrm{ax}},\\(\nu_2-\nu_0)\nu_0^{-1}&=\Delta\nu_2/\nu_0=\delta_{\mathrm{is}}-\delta_{\mathrm{ax}}+\delta_{\mathrm{asym}},\\(\nu_3-\nu_0)\nu_0^{-1}&=\Delta\nu_3/\nu_0=\delta_{\mathrm{is}}-\delta_{\mathrm{ax}}-\delta_{\mathrm{asym}},\end{aligned}\quad(4)$$

δ_{is} is the relative isotropic shift. For positions of axial symmetry $\delta_{\mathrm{asym}}=0$, for positions of cubic symmetry $\delta_{\mathrm{ax}}=0$. The terms in δ_{ax} and δ_{asym} will make a contribution to the second moment, which is proportional to the square of the resonance frequency ν_0 and independent of the dipolar and exchange contributions.

A priori we have no knowledge of the quantities $\tilde{A}$ and $\tilde{B}$ which have been introduced in a strictly phenomenological way. Anticipating results of the final sections, it is assumed that their magnitude decreases very rapidly with distance between the two components of a pair. In fact they decrease exponentially with r in an insulator, and they decrease as rapidly as the dipolar interaction in the metal, or proportional to r^{-3}. We shall therefore restrict the sums to the twelve nearest neighbors ($z=12$) in both the metal and the oxide. In the former the omission of further lattice sites will introduce an error of about 20 percent as a quantitative evaluation of the complete pure dipolar sum for the thallium lattice shows. The error in the oxide for the exchange and pseudo-dipolar contributions is much smaller than this.

It will also become clear from the atomic theory of exchange between a nuclear spin pair, that the interactions are proportional to the g-factors of the two nuclei:

$$\begin{aligned}\tilde{A}_{ij}&=gg'^{-1}\tilde{A}_{ij'}=g^2g'^{-2}\tilde{A}_{i'j'},\\\tilde{B}_{ij}&=gg'^{-1}B_{ij'}=g^2g'^{-2}B_{i'j'}.\end{aligned}$$

Since $(g-g')/g\sim 1$ percent, it is assumed $gg'^{-1}=1$. Furthermore it is assumed that all twelve nearest neighbors are equivalent which is true for a fcc lattice, but is an approximation for the actual thallium and $\mathrm{Tl_2O_3}$ lattices. In taking the numerical values of g and g' equal for computational purposes, it should be kept in mind that their difference, however small, is responsible for the important distinction between like and unlike spins.

If two different isotopes happened to have the same g-value, they should be considered as equivalent neighbors in the context of this paper and exchange broadening would not occur. It cannot be overemphasized that the Pauli exclusion principle between identical particles and related concepts do not enter into the discussion of nuclear spin exchange. The spin orientation only of the nuclei, whose orbits never overlap, is exchanged via intermediate electrons.

Introducing the relative concentration f for Tl^{203} and $1-f$ for Tl^{205} in the completely random mixture of isotopes, the second moment expression (2) for the Tl^{205} resonance with respect to its center of gravity,

$$\nu_c = g\beta h^{-1} H_{\text{ext}}(1+\delta_{\text{is}}), \tag{5}$$

becomes for $z=12$ nearest neighbors at a distance a,

$$\langle \Delta\nu^2 \rangle_{\text{Av}} = g^2\beta^2 h^{-2} H^2 \left[\frac{4}{5}\delta_{\text{ax}}{}^2 + \frac{4}{15}\delta_{\text{asym}}{}^2 \right] + 3f\tilde{A}^2 + \left\{ \frac{12}{5}f + \frac{27}{5}(1-f) \right\} (\tilde{B} + g^2\beta^2 a^{-3})^2. \tag{6}$$

This formula will be used to interpret the observed values of the second moment.

(b) Line Shape and Fourth Moment

Van Vleck has given a complete expression for the fourth moment, but this quantity cannot be determined experimentally with any precision. The following discussion of two limiting cases proceeds along the same lines as Kittel's argument.[14]

Extreme exchange broadening, $|f^{\frac{1}{2}}\tilde{A}| \gg |\tilde{B} + g^2\beta^2 a^{-3}|$. The dominant terms in the fourth moment are those in $\tilde{A}^4$. With the same simplifying assumptions this dominant term is found from Van Vleck's general expression to be

$$\langle \Delta\nu^4 \rangle_{\text{Av}} \approx (9/4)(5f + 11f^2)\tilde{A}^4 h^{-4}. \tag{7}$$

Using only the dominant term $3f\tilde{A}^2$ in the expression for the second moment, one obtains

$$\begin{aligned} [\langle \Delta\nu^4 \rangle_{\text{Av}}]^{\frac{1}{4}} / [\langle \Delta\nu^2 \rangle_{\text{Av}}]^{\frac{1}{2}} &= 1.41 \quad \text{for} \quad f=1 \\ &= 1.51 \quad \text{for} \quad f=0.5 \\ &= 1.66 \quad \text{for} \quad f=0.25 \\ &= 1.94 \quad \text{for} \quad f=0.1. \end{aligned}$$

The ratio would be 1.32 for a Gaussian distribution. For small f the fourth moment tends to dominate the square of the second moment. This is the dilution effect, discussed by Abraham and Kittel. For $f=0.1$, however, the dipolar terms become of equal importance with the exchange broadening terms, and a more potent narrowing mechanism will take over. Exchange narrowing dominant, $|f^{\frac{1}{2}}\tilde{A}| \ll |\tilde{B} + g^2\beta^2 a^{-3}|$, but $|\tilde{A}| > |\tilde{B} + g^2\beta^2 a^{-3}|$. This limiting case is identical with the exchange narrowing for one isotopic constituent considered by Van Vleck,

$$\frac{[\langle \Delta\nu^4 \rangle_{\text{Av}}]^{\frac{1}{4}}}{[\langle \Delta\nu^2 \rangle_{\text{Av}}]^{\frac{1}{2}}} \approx \frac{\tilde{A}}{\tilde{B} + g^2\beta^2 a^{-3}}. \tag{8}$$

For extreme narrowing, when this ratio is large compared to unity, the line assumes a Lorentzian shape near the center,

$$f(\nu) = \{1 + (\nu - \nu_c)^2 \Delta\nu_{\text{eff}}{}^{-2}\}^{-1},$$

with an effective half-width

$$\Delta\nu_{\text{eff}} = \tfrac{1}{2}\sqrt{3}\,\Delta\nu_{msl} = \frac{h\langle \Delta\nu^2 \rangle_{\text{Av}}}{z^{\frac{1}{2}} A\lambda}. \tag{9}$$

If this Lorentzian is cut off at a frequency

$$\nu_{\text{co}} = \lambda(\pi/2) z^{\frac{1}{2}} A h^{-1}, \tag{10}$$

the correct value for the second moment is obtained. The numerical constant λ is of the order of unity. Its actual value depends on the detailed model of exchange narrowing.[15]

(c) Line Shape and Anisotropy of the Chemical Shift

It was already mentioned that the line shape in the oxide for $f \ll 1$ is predominantly determined by the anisotropy of the shift rather than the exchange narrowing. The problem of the line shape in powder samples due to anisotropy in the resonance condition has already been solved elsewhere by the authors.[1] The same solution applies to powder line patterns in the presence of anisotropic g-factors and quadrupole broadening in fields of nonaxial symmetry. Since an incorrect line shape has been published in this Journal,[16] the derivation will be outlined briefly, in a slightly improved form. The resonance frequency is given by

$$\nu^2 = \nu_1{}^2 \cos^2\theta + \nu_2{}^2 \sin^2\theta \cos^2\phi + \nu_3{}^2 \sin^2\theta \sin^2\phi. \tag{11}$$

Without loss of generality it is assumed that $\nu_1 > \nu_2 > \nu_3$, and these quantities are given by Eq. (4). The polar angles θ and ϕ determine the direction of the field H with respect to the axes of the resonance frequency ellipsoid. When the differences between ν_1, ν_2, and ν_3 are small, Eq. (11) reduces to

$$\nu = \nu_1 \cos^2\theta + \nu_2 \sin^2\theta \cos^2\phi + \nu_3 \sin^2\theta \sin^2\phi. \tag{12}$$

Transform from the variables θ and ϕ, to the set ν and $\theta = \theta'$. The line shape in a powder is given by

$$\mathcal{g}(\nu) = \int_{\text{real values}} \frac{\partial(\phi,\theta)}{\partial(\nu,\theta)} \sin\theta d\theta.$$

The limits of integration are determined by the condition of physical reality. The integration is to be extended over all real values of θ which are compatible with a given real value of ν. The final result can be

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[14] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953); M. A. Ruderman and C. Kittel, reference 6.

[15] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

[16] C. Kikuchi and V. W. Cohen, Phys. Rev. **93**, 394 (1954).

brought into the form of the tabulated[17] complete elliptic integral $K(\sin\alpha)$. The normalized line shape functions are

$$f(\nu)=\pi^{-1}(\nu-\nu_3)^{-\frac{1}{2}}(\nu_1-\nu_2)^{-\frac{1}{2}}K(\sin\alpha)$$

with (13)

$$\sin^2\alpha=(\nu_2-\nu_3)(\nu_1-\nu)/(\nu_1-\nu_2)(\nu-\nu_3) \text{ for } \nu_1>\nu>\nu_2,$$

$$f(\nu)=\pi^{-1}(\nu_1-\nu)^{-\frac{1}{2}}(\nu_2-\nu_3)^{-\frac{1}{2}}K(\sin\alpha)$$

with

$$\sin^2\alpha=(\nu-\nu_3)(\nu_1-\nu_2)/(\nu_1-\nu)(\nu_2-\nu_3) \text{ for } \nu_2>\nu>\nu_3,$$

$$f(\nu)=0 \qquad \text{for } \nu>\nu_1 \text{ or } \nu<\nu_3.$$

For axial symmetry $\nu_3=\nu_2$, the shape function reduces properly to

$$f_{\text{ax}}(\nu)=\tfrac{1}{2}(\nu_1-\nu_2)^{-\frac{1}{2}}(\nu-\nu_2)^{-\frac{1}{2}}. \tag{14}$$

These theoretical shapes are shown as dotted curves in Fig. 2.

Equations (13) and (14) have to be replaced by more complicated expressions, if the relative shifts are not small. Equation (11) has to be used instead of (12). To obtain the distribution of nuclei over the resonant frequencies ν, every frequency in (13) and (14) has to be replaced by its square and a factor 2ν must be added. The final expression for the intensity distribution should also take into account that the radio-frequency field is not quite perpendicular to the internal field, but makes an angle χ. For each crystalline orientation one has to multiply by $\sin^2\chi$, which may be expressed in terms of θ and ϕ. For large axial anisotropy, Eq. (14) has to be replaced by the powder line shape function,

$$f_{\text{ax}}(\nu)=\nu(\nu_1^2-\nu_2^2)^{-\frac{1}{2}}(\nu^2-\nu_2^2)^{-\frac{1}{2}} \times\left(1-\frac{(\nu^2-\nu_2^2)(\nu_1^2-\nu^2)}{2\nu^2(\nu_1+\nu_2)^2}\right). \tag{15}$$

(d) Line Shape in Small External Fields

Finally, we turn to the question of the line shape in small external fields, when the exchange interaction becomes comparable with the difference of the unperturbed energies. Van Vleck's expressions do not apply to this case, as the Hamiltonian has to be truncated in a different manner, when $A_{jk'}>(g-g')\beta H$. The exchange between like spins commutes with the total Zeeman energy, but the exchange between unlike pairs does not so commute. The two spins in a pair would be considered as nonequivalent if $g_1H_1\neq g_2H_2$. If the exchange energy between such a pair of nuclear spins with different g-values in the same field or the same g-value in different fields is small, the problem can be treated by a perturbation procedure, i.e., the Hamiltonian can be truncated in the usual manner described in Van Vleck's paper.

The problem of large exchange between nonequivalent spins is a difficult one. In the limit of very large exchange one could follow Pryce[18] and consider the difference in the spins as a small perturbation. The Hamiltonian, from which we omit the dipolar interactions to avoid lengthy computations, can be split in the following manner:

$$\mathcal{H}_z+\mathcal{H}_{\text{ex}}=\beta[fgH+(1-f)g'H'](\textstyle\sum_jI_{zj}+\sum_{k'}I_{zk'})+\mathcal{H}_{\text{ex}} +\beta(gH-g'H')[(1-f)\textstyle\sum_jI_{zj}-f\sum_{k'}I_{zk'}]. \tag{16}$$

The interaction with the radio-frequency field was formerly split into the contributions of two different species. This should also be changed:

$$\begin{aligned}\beta H_{\text{rf}}(g\textstyle\sum_jI_{xj}+g'\sum_{k'}I_{xk'}) &=\beta H_{\text{rf}}\{\tfrac{1}{2}(g+g')(\textstyle\sum_jI_{xj}+\sum_{k'}I_{xk'})\}\\ &\quad+[\tfrac{1}{2}\beta H_{\text{rf}}(g-g')(\textstyle\sum_jI_{xj}-\sum_{k'}I_{xk'})].\end{aligned} \tag{17}$$

The operator between square brackets will always change the sign of the exchange energy between unlike spins. It produces satellite absorption at frequencies of the magnitude of the exchange frequency and will henceforth be omitted. The commutator of the first term on the left-hand side of (17) with the Hamiltonian (16) can now be calculated, and expressions for the second and fourth moments derived, using Van Vleck's Eqs. (7–10) and (17):

$$\langle\Delta\nu^2\rangle_{\text{Av}}=h^{-2}\beta^2(gH-g'H')^2f(1-f). \tag{18}$$

Here $\Delta\nu=\nu-\nu_c$, where the centroid frequency is given by

$$\nu_c=h^{-1}\beta\{fgH+(1-f)g'H'\}. \tag{19}$$

In writing the Hamiltonian (16), this result was anticipated so that $\langle\Delta\nu^2\rangle_{\text{Av}}$ is minimized. The simplification that all spins have the same total angular momentum, I, has been made. The expression for the fourth moment becomes

$$\begin{aligned}\langle\Delta\nu^4\rangle_{\text{Av}}&=h^{-4}\beta^4(gH-g'H')^4\{f^4(1-f)+(1-f)^4f\}\\ &\quad+(gH-g'H')^2A^2f(1-f)z\tfrac{2}{3}I(I+1),\end{aligned} \tag{20}$$

$$\begin{aligned}\langle\Delta\nu^4\rangle_{\text{Av}}&=\langle\nu^4\rangle_{\text{Av}}-\nu_c^4-6\nu_c^2\langle\Delta\nu^2\rangle_{\text{Av}}\\ &\quad-4\beta^3h^{-3}(gH-g'H')^3\nu_cf(1-f)(1-2f).\end{aligned}$$

It has been assumed that the exchange interaction has the value A for z nearest neighbors, and vanishes for all other pairs. The last term gives a measure for the asymmetry of the absorption around the centroid. It vanishes properly when $f=\frac{1}{2}$, since a symmetrical absorption pattern should result, when the two isotopes occur in equal concentration.

The dominant term is the second term on the right-hand side and the fourth moment is seen to be larger than the square of the second moment by a factor of the order $zA^2/(gH-g'H')^2$. In analogy with the dipolar exchange narrowing, one may interpret this that there is a narrow line at the centroid position with an effective

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[17] E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, Inc., New York, 1945), pp. 52–85.

[18] M. H. L. Pryce, Nature **162**, 538 (1948).

width $(gH-g'H')^2/Az^{\frac{1}{2}}$. In the simple case of just two spins it is easily verified that in the limit of large exchange the absorption spectrum consists of a pair of lines, each a distance $(gH-g'H')^2/4A$ from the central position.

Considerable care should however be exercised, as a finite absorption over a region $(gH-g'H')\hbar^{-1}\beta$ cannot generally be excluded by the calculation of the moments alone. The example of the case of three spins, two of which are identical with gyromagnetic ratio $g_1=g_2=g$ while the third one has g_3, illustrates this. A complete quantum mechanical solution can be given in this case.[3] Our interest is in the situation for very large exchange energy between the unlike spins $A(\mathbf{I}_1+\mathbf{I}_2)\cdot\mathbf{I}_3$. For $A\rightarrow\infty$, the absorption spectrum consists of three lines, one at the average position $(\frac{2}{3}g+\frac{1}{3}g_3)\hbar^{-1}\beta H$ and two satellites symmetrically located at $[(4/3)g-\frac{1}{3}g_3]\times\hbar^{-1}\beta H$ and $g_3\hbar^{-1}\beta H$. The intensities of these lines are in the ratio 4:90:9. Thus no definite conclusions can be drawn from the calculation of second and fourth moments alone, unless the truncation process of Eqs. (16) and (17) can be refined. This is even more true if the exchange interaction is not large, but comparable to the difference in Zeeman energies. To obtain a semiquantitative idea what can be expected in this case, refuge is taken to less rigorous, approximate methods.

A well known approximation in exchange problems is the introduction of an effective field. Consider the resultant magnetization $\mathbf{M}$ of the unprimed variety and $\mathbf{M}'$ of the primed variety. In the absence of exchange between mixed pairs these will precess independently in the magnetic field H. The exchange coupling between $\mathbf{M}$ and $\mathbf{M}'$ is taken into account by an effective field $\lambda\mathbf{M}'=A\mathbf{M}'/g_1g_2\beta^2$ acting on $\mathbf{M}$, and $\lambda\mathbf{M}$ acting on $\mathbf{M}'$. The equations of motion for the two spin systems become

$$d\mathbf{M}/dt=\hbar^{-1}g\beta\{\mathbf{M}\times(\mathbf{H}+\lambda\mathbf{M}')\},$$
$$d\mathbf{M}'/dt=\hbar^{-1}g\beta'\{\mathbf{M}'\times(\mathbf{H}'+\lambda\mathbf{M})\},$$

with the two eigenfrequencies

$$\begin{aligned}\nu=&\tfrac{1}{2}(gH+g'H')\beta\hbar^{-1}+\tfrac{1}{2}\beta\hbar^{-1}(g'M_z+gM_z')\\&\pm\tfrac{1}{2}\beta\hbar^{-1}[(gH-g'H')^2+2(gH-g'H')(gM_z'-g'M_z)\lambda\\&+\lambda^2(g'M_z+gM_z')^2]^{\frac{1}{2}}.\end{aligned}\qquad(21)$$

This approach has been used frequently to discuss the ferromagnetic resonance of the two spin systems in ferrites.[19] In the case of large exchange it gives the correct resonance condition at the "average" frequency:

$$\nu=\{fgH+(1-f)g'H'\}\beta\hbar^{-1},$$

with

$$f=g'M_z(g'M_z+gM_z')^{-1}.$$

Above the Curie point the omission of the fluctuations in the exchange fields, i.e., of terms quadratic in the transverse components of the spins, is however very serious. The solution (21) gives erroneous results for the nuclear two-spin system, where the average exchange fields are small compared to the fluctuations.

In order to obtain a better idea about the change in absorption for intermediate values of the nuclear spin exchange, it is assumed that the system can be represented by a model of a rotating magnetization which changes at random intervals from the frequency $\nu_0=gH\beta\hbar^{-1}$ to the frequency $\nu_0'=g'H'\beta\hbar^{-1}$ and vice versa. The magnetization is a continuous function of time. The fluctuating exchange fields are responsible for the transitions which have a probability per unit time of the order of the exchange frequency. Such a model has been discussed by Slichter,[20] by Archer[21] and by Anderson[16] with three entirely different mathematical methods. They all discuss the case that the oscillator or rotating magnetization spends equal time at the two frequencies, and the transition probability to jump from ν_0 to ν_0' or ν_0' to ν_0 is the same. Anderson and Archer derive the spectral distribution from the correlation function for the freely radiating oscillator, whereas Slichter starts from the magnetization driven by an external harmonic field. Slichter's method is by far the simplest and covers in addition the case that the oscillator is subjected to other external damping mechanisms at each of the two frequencies. Furthermore his method can be readily extended[22] to the situation that the oscillator spends a fraction f of the time at frequency ν and a fraction $f'=1-f$ at the frequency ν', corresponding to the fractions of the primed and unprimed isotope. The transition probability for a frequency jump is assumed to be proportional to the probability f or f' of the oscillator frequency after the transition:

$$\begin{aligned}\tau^{-1}&=|A|\hbar^{-1}z^{\frac{1}{2}}(1-f),\\\tau'^{-1}&=|A|\hbar^{-1}z^{\frac{1}{2}}f.\end{aligned}\qquad(22)$$

Unfortunately the numerical factor cannot be derived in a rigorous manner and is assumed to be unity.

The generalization of Slichter's equation for the absorption curve is

$$\mathcal{g}(\nu)\propto\mathrm{Re}\frac{\tau+\tau'+(\tau^{-1}+\tau'^{-1})^{-1}(\alpha\tau'+\alpha'\tau)}{(1+\alpha'\tau')(1+\alpha\tau)-1},\qquad(23)$$

with

$$\begin{aligned}\alpha&=T_2^{-1}-2\pi i(\nu-\nu_0),\\\alpha'&=T_2'^{-1}-2\pi i(\nu-\nu_0').\end{aligned}\qquad(24)$$

In the limit of large exchange $\tau\rightarrow0$, a single narrow resonance at the average frequency results. For $\tau\rightarrow\infty$ two separate resonances occur. T_2^{-1} and $T_2'^{-1}$ represent the widths the separate resonances would have, if there were no frequency jumps. T_2 and τ should be of the same order of magnitude, but the ratio is not deter-

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[19] See, e.g., R. K. Wangsness, Phys. Rev. **91**, 1085 (1953). Further references to the literature are given in this paper.

[20] Gutowski, McCall, and Slichter, reference 4. [Eq. (41).]

[21] D. H. Archer, thesis, Harvard University, 1953 (unpublished).

[22] H. S. Gutowski and A. Saika, J. Chem. Phys. **21**, 1688 (1953).

mined in this model. It is believed that Eqs. (22)–(24) give a fairly reliable description for intermediate values of the exchange coupling, although the model is strictly not applicable. For $T_2^{-1}=T_2'^{-1}=0$ and $\tau=\tau'$ Eq. (23) reduces to the shape function of Archer-Anderson:

$$\mathcal{G}(\omega)d\omega=\frac{\omega_e\omega_0^2}{\omega^4+2\omega^2(2\omega_e^2-\omega_0^2)+\omega_0^4}, \tag{25}$$

with

$$\omega=2\pi[\nu-\tfrac{1}{2}(\nu_0+\nu_0')],$$
$$\omega_0=2\pi\tfrac{1}{2}(\nu_0-\nu_0'),$$
$$\omega_e=\tau^{-1}.$$

IV. COMPARISON OF THEORY AND EXPERIMENT

With the aid of the formulas developed in the preceding sections the experimental results may now be used to obtain numerical values for the phenomenological quantities introduced.

TABLE IV. Contributions to the second moment of the Tl^{203} and Tl^{205} resonances in Tl_2O_3. All $\langle\Delta\nu^2\rangle_{Av}$ contributions are in units $(kc/sec)^2$.

Abundance (percent)	Magnetic field in gauss	Dipolar and pseudo-dipolar	Aniso-tropic shift	Ex-change	Total theory	Ob-served	Classical dipolar alone
98.7 Tl^{205}	5560	<9	60	5.4	70	70	4.5
98.7 Tl^{205}	3288	<9	22	5.4	32	35	4.5
90.5 Tl^{205}	5560	<8.6	60	39	104	91	4.3
90.5 Tl^{205}	3288	<8.6	22	39	66	54	4.3
70.5 Tl^{205}	5560	<7.6	60	121	185	196	3.8
52.1 Tl^{205}	5560	<6.6	60	220	285	290	3.3
14.0 Tl^{205}	5560	<4.6	60	353	415	>400	2.3
86 Tl^{203}	5560	<8.2	60	65	130	118	4.1
47.9 Tl^{203}	5560	<6.6	60	240	305	310	3.3
29.5 Tl^{203}	5560	<5.0	60	320	383	360	2.5

The best starting point for the discussion is the observation of the second moment in the nearly pure isotope, 98.7 percent Tl^{205}. One can put $f=0$ in Eq. (6). Minor corrections because $f=0.013$ can be made afterwards. The second moment consists of a field-independent contribution from the dipolar or pseudo-dipolar broadening and a contribution from the anisotropy which is proportional to the square of the field. These two contributions can be separated because observations at two different field strengths are available. It turns out that for the oxide the anisotropy is so much larger than the dipolar contribution, that only an upper limit can be given for the magnitude of the latter. In the metal the pseudo-dipolar interaction is dominant, but an anisotropy of the Knight shift is still noticeable (compare Fig. 4). The anisotropy broadening is not affected by exchange, but the dipolar part will be exchange-narrowed. In order to obtain the correct contribution to the second moment the line must be integrated from the center to a distance of the order of the exchange frequency, Eq. (10), or to about 40 kc/sec in our samples. It is difficult to obtain reliable values for the contributions from the tails and the pseudo-dipolar second moment may be somewhat underestimated. Fortunately the exchange narrowing is not severe, especially not in the metal, where the effective "narrowing factor" Eq. (8) is about two. This figure is estimated from the ratio of experimental widths of the Tl^{205} resonance in 98.7 percent and 14 percent Tl^{205} sample. If there were no pseudo-dipolar interaction, the narrowing factor would have been 14 and the line shape would have been determined entirely by the anisotropy. The observed second moment in the 50 percent composition serves to determine the exchange constant A, which is the remaining unknown parameter in Eq. (6). Then this equation can be used to calculate the second moment for the Tl^{203} and Tl^{205} resonances in all other compositions and at other field strengths. The results for the oxide are compiled in Table IV, for the metal in Table V. It is seen that very good agreement with experimental values in the next to last column is obtained. For purposes of comparison the last column contains the contribution from the classical dipolar interaction alone, which thus far was usually considered the important broadening agent in solids. Its inadequacy in the present case is striking.

The numerical values for the exchange interactions between nearest neighbors in the oxide can be found from Table IV and Eq. (6). They are

$$|A|h^{-1}=12 \text{ kc/sec}, \quad -2.2<Bh^{-1}<0.35 \text{ kc/sec}.$$

This latter ambiguity arises from the fact that there may be constructive or destructive interference with the ordinary dipolar interaction. Neither can the sign of A be determined by these experiments. An independent determination of the exchange interaction is possible from the inward shift of the resonance at lower field strength with the aid of Eqs. (23) or (25). In Fig. 3 the integrated experimental line is compared with these theoretical expressions. The dotted curve (a) corresponds to Eq. (23), and the dotted curve (b) to Eq. (25). The distance between the maxima of absorption is reduced to 79 percent of the distance of the unperturbed Tl^{203} and Tl^{205} resonances. This determines τ. If one takes $\pi\tau(\nu_0'-\nu_0)=2.38$, the theoretical curves give the correct position of the maxima. With Eq. (22) this value of τ leads to $|A|h^{-1}=9.6$ kc/sec in fair agreement with the value derived from the second moment. The discrepancy is undoubtedly due to the uncertainty in the numerical factors. The value $|A|h^{-1}=12$ kc/sec

TABLE V. Contributions to the second moment of the Tl^{205} resonance in thallium at 77°K. All contributions to $\langle\Delta\nu^2\rangle_{Av}$ are in units $(kc/sec)^2$.

Abundance (percent)	Magnetic field in gauss	Dipolar and pseudo-dipolar	Aniso-tropic shift	Ex-change	Total theory	Ob-served	Classical dipolar alone
98.7 Tl^{205}	5560	200	100	14	314	300	6.2
	3288	200	35	14	249	220	6.2
90.5 Tl^{205}	5560	189	100	102	391	395	5.9
	3288	189	35	102	326	280	5.9
70.5 Tl^{205}	5560	170	100	312	592	590	5.3
	3288	170	35	312	517	590	5.3
52.1 Tl^{205}	5560	148	100	570	818	820	4.6
14.0 Tl^{205}	5560	105	100	910	1105	?	3.3

is more reliable and should be retained. Curve (a) gives much better agreement with experiment, since it includes the additional broadening T_2^{-1}, not associated with frequency transitions. The very good fit was obtained by taking $\tau/T_2=0.6$.

To evaluate the exchange constants for nearest neighbors in the metal, twenty percent is subtracted from the contribution of the exchange and dipolar broadening to account approximately for the effect of farther neighbors. Then Eq. (6) gives the following values $|A|=17.5$ kc/sec and $B=+4.5$ or -6.5 kc/sec, as compared to the classical dipolar constant $g^2\beta^2a^{-3}=1$ kc/sec. At the lower field strength in the 50 percent–50 percent composition of the metal $\pi\tau(\nu_0'-\nu_0)=1.42$, which results in a broad unobservable line shape. The anisotropy of the shift in the hexagonal metal amounts to $\delta_{\text{ax}}=0.08$ percent. Consequently, the anisotropy in the Knight shift

$$(\Delta\nu_{\parallel}-\Delta\nu_{\perp})/\Delta\nu_{\text{is}}=0.24\text{ percent}/1.56\text{ percent}=16\text{ percent}.$$

The evaluation of the anisotropy constants for the shift in the oxide is much more complicated. In the powder specimen one is clearly not concerned with the orientation of the shift ellipsoids in the crystal. Only the axial ratios of the ellipsoids are important, but the oxide has two different types of thallium atoms in the unit cell. Eight atoms on the body diagonal have ellipsoids with rotational symmetry and require one anisotropy constant. Twenty-four atoms of lower symmetry have other ellipsoids, all with the same axial ratios. This requires two additional constants. Furthermore it is conceivable that the isotropic shift of the atoms of first kind is not the same as for the atoms of the second kind. This would lead to an additional contribution to the second moment, which has not been considered before in this paper. Clearly the experimental curve of Fig. 2 cannot yield these four independent constants. Experiments at much higher field strengths would be necessary to give a better determination of the line shape. Data on single crystals would hardly be more revealing. For an arbitrary orientation of the external field there would be sixteen different resonance curves! This difficulty is inherent in the large number of atoms in the unit cell.

We have tried to fit the experimental curve as well as possible with a line shape of axial symmetry alone [Eq. (14), dotted curve in Fig. 2] and separately for a line shape for less than axial symmetry [Eq. (13), dashed curve in Fig. 2]. It is seen that 75 percent of the latter curve and 25 percent of the former gives an extremely good fit with the experimental shape. In the case of axial symmetry the anisotropy parameter is determined by the second moment alone $\delta_{\text{ax}}=0.063$ percent. This gives an anisotropy of the chemical shift

$$(\Delta\nu_{\parallel}-\Delta\nu_{\perp})/\Delta\nu_{\text{is}}=0.19/0.55=34\text{ percent}.$$

In the case of lower symmetry the two parameters are determined by the second moment and the shift of the center of gravity of the line with respect to the maximum using (4) and (6) one finds $\delta_{\text{ax}}=0.061$ percent and $\delta_{\text{asym}}=0.03$ percent. The uncertainty in these numbers is rather large, especially in δ_{asym}. Yet it can be said that conclusive evidence for the anisotropy of a chemical shift has been found, and that the anisotropy has some nonaxial symmetry.

The influence of exchange between the Tl^{205} nuclei with different chemical shifts has been ignored in this discussion. If the exchange interaction were very large compared to the difference in chemical shifts an average resonance frequency for all thallium atoms in the unit cell would be observed. Since the unit cell is cubic, this average would show no anisotropy. The experimental results indicate that the exchange interaction does not produce such a complete averaging. Its influence at the higher magnetic field is probably small, but at the lower field the exchange energy and the difference in chemical shifts are comparable. It seems a hopeless task to treat the exchange interaction between the various nonequivalent Tl^{205} nuclei in the unit cell adequately. This points again to the desirability to investigate the anisotropy of the chemical shift in simpler structures.

It has been shown that all experimental data can be interpreted satisfactorily in terms of the phenomenological theory. This interpretation indicates that the discussion of the Knight shift in thallium and its alloys as given in a previous paper (reference 1) remains essentially unchanged. The broadening of the line in alloys may in part be due to exchange between unlike nuclei. The shifts at the lower field strength reported in reference 1, are not reliable, however, because of the coalescence of the two thallium resonances at low fields.

The gradual change in shape from Gaussian to Lorentzian with increasing concentration of like neighbors has been discussed before. It is in semiquantitative agreement with Eqs. (7), (8), and (9). It remains to be shown that the numerical values, found for the exchange constants A and B, are reasonable ones in terms of an atomistic theory.

V. ATOMISTIC THEORY OF NUCLEAR SPIN EXCHANGE COUPLING IN SOLIDS

Ramsey and Purcell have shown that the nuclear spin-electron spin interaction will give rise in second-order perturbation theory to an exchange-type of coupling between nuclear spins in molecules. Ramsey's theory for this type of interaction in molecules can readily be extended to periodic lattices. Ruderman and Kittel have already given the extension for the nuclear spin coupling by the conduction electrons in a metal. The analogous process for coupling in an insulator via excited electron states will be derived here along similar lines.

The electrons in the solid may be adequately described by one-electron wave functions of the Bloch type,[23] normalized over a large volume V:

$$\psi_{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}),\quad V^{-1}\int\psi_{\mathbf{k}}^*\psi_{\mathbf{k}}d\tau=1. \tag{26}$$

$u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice.[24] Exchange and correlation effects are neglected in this treatment.

A pair of nuclear spins is introduced at positions $\mathbf{R}_i$ and $\mathbf{R}_j$ in the lattice. The perturbation of the wave function by the nuclear spin-electron spin interaction is considered,

$$\begin{aligned}\mathcal{H}_{I_iS}=\frac{16\pi}{3}\beta g_N\beta_N\mathbf{I}_i\cdot\mathbf{S}\delta(\mathbf{r}_i)+2\beta g_N\beta_N&\\ \times\mathbf{I}_i\cdot\{\mathbf{S}r_i^{-3}-3r_i^{-5}(\mathbf{S}\cdot\mathbf{r}_i)\mathbf{r}_i\},&\end{aligned} \tag{27}$$

where $\mathbf{r}_i=\mathbf{r}-\mathbf{R}_i$ is the radius vector from the nucleus i to the electron. The Bohr magneton β has a negative value. The nuclear spin j produces a similar interaction.

The second term represents the classical dipolar interaction between two dipoles. It was omitted in Kittel's paper. It will be shown to be responsible for the pseudo-dipolar interaction in the next section. For the time being consider only the first term. When the wave function has a finite value at the nucleus, there is an interaction corresponding to the hyperfine structure in atomic S-states. In second-order perturbation theory the change in energy of the system due to the Hamiltonian (27) is

$$\begin{aligned}\textstyle\sum_{\mathrm{k}'}\sum_{s'}(\psi_{\mathrm{k}'}^*s'|\mathcal{H}_{IS}|\psi_{\mathrm{k}}s)(\psi_{\mathrm{k}}^*s|\mathcal{H}_{IS}|\psi_{\mathrm{k}'}s')&\\ \times\{E(\mathbf{k})-E(\mathbf{k}')\}^{-1}.&\end{aligned}$$

The summation is over all excited states $\mathbf{k}'$ and the two spin orientations $\mathbf{s}'$. The interest is in terms which depend on both nuclear spins. The transition to the intermediate excited state is due to spin i and the transition back to the ground state due to spin j, or the role of i and j is reversed. To obtain the total energy perturbation caused by the introduction of nuclear spins i and j, the summation over all initially occupied states $\mathbf{k}$, $\mathbf{s}$ has to be performed. The three-dimensional δ function in (27) makes the evaluation of the matrix elements simple. The summation over the two electron spin orientations in the initial and intermediate states can also be performed readily. The integration over the volume V cancels the normalization factor in (26) and the result is

$$\begin{aligned}\mathcal{H}_{ij}^{\mathrm{exch}}=\mathbf{I}_i\cdot\mathbf{I}_j[2\,\mathrm{Re}\textstyle\sum_{\mathrm{k}}\sum_{\mathrm{k}'}\Delta_i(k,k')&\\ \times\Delta_j(k',k)e^{i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_i-\mathbf{R}_j)}\{E(\mathbf{k})-E(\mathbf{k}')\}^{-1}],&\end{aligned} \tag{28}$$

with

$$\begin{aligned}\Delta_i(k,k')&=\Delta_i^*(k',k)\\ &=(16\pi/3)g_N\beta_N\beta u_{\mathrm{k}}(\mathbf{R}_i)u_{\mathrm{k}'}^*(\mathbf{R}_i).\end{aligned} \tag{29}$$

The complex conjugate is added because the role of i and j can be interchanged, resulting in twice the real part. The expression between square brackets in (28) represents the previously introduced quantity A_{ij} and is generally valid for all periodic lattices. The difference, e.g., between metals and insulators becomes apparent in the evaluation of the sums over all occupied initial states $\mathbf{k}$ and all unoccupied intermediate states $\mathbf{k}'$. To gain insight into the magnitude of the quantity A_{ij} some simplifying assumptions about the $\mathbf{k}$-dependence of the integrand will be made. These restrictions are not essential and many refinements on them could be introduced. More complicated integrals would then have to be evaluated.

For the case of an insulator the assumption is made that the occupied band is narrow compared to the gap between the top of this band and the bottom of the conduction band, and that this gap is uniform for all directions $E_g\gg E_k$. The energy of a conduction electron in this band and all higher bands is represented by $E_{k'}=k'^2\hbar^2/2m'$, where k' assumes the value 0 at the bottom of the band and runs to infinity, m' is the effective mass. Lower filled bands are assumed to have such a large energy difference with the conduction band that their contribution is neglected. With these approximations one has

$$E_{k'}-E_k=E_g+k'^2\hbar^2/2m'. \tag{30}$$

Furthermore a suitable average,

$$\langle\Delta_i(kk')\Delta_j(kk')\rangle_{\mathrm{eff}}=(|\Delta_{ij}|^2)_{\mathrm{Av}}, \tag{29a}$$

over the two bands is introduced. This is not simply the arithmetic mean, as the quantities are weighted with the inverse energy difference between the two states. With these simplifications the integrations over $\mathbf{k}$ and $\mathbf{k}'$ can be carried out in spherical coordinates.

If one writes $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$, the result of the angular integrations is

$$\begin{aligned}A_{ij}=-(|\Delta_{ij}|^2)_{\mathrm{Av}}\tfrac{1}{4}m'\hbar^{-2}\pi^{-4}R_{ij}^{-2}\int_0^{k_t}\sin(kR_{ij})kdk&\\ \times\int_0^{\infty}\sin(k'R_{ij})k'[k'^2+2mE_g\hbar^{-2}]^{-1}dk'.&\end{aligned}$$

The last integral can be evaluated by contour integration in the complex plane and gives an exponential factor. The upper limit of the first integral is the top of the filled band. For a Wigner-Seitz sphere of atomic volume v_a, which accommodates one electron of given spin orientation, one has

$$k_t=2\pi(3/4\pi v_a)^{\frac{1}{3}}. \tag{31}$$

The spherical approximation is clearly not valid near the zone boundaries, but it allows for a simple evalua-

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[23] See, e.g., F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 348 ff.

[24] In subscripts k and k′ will often stand for $\mathbf{k}$ and $\mathbf{k}'$.

tion of the integral and is consistent with earlier approximations. The final result is

$$A_{ij}=-\tfrac{1}{4}(|\Delta_{ij}|^2)_{\mathrm{Av}}\, m'\hbar^{-2}\pi^{-3}R_{ij}^{-4}[\sin(k_tR_{ij}) - k_tR_{ij}\cos(k_tR_{ij})]\exp\{-\hbar^{-1}(2m'E_g)^{\frac{1}{2}}R_{ij}\}. \qquad (32)$$

In the case of a metal there is no energy gap and a conduction electron near the top of the Fermi distribution may be scattered into a state with approximately the same energy. The integration over k is now from zero to k_m, the value of the wave number at the Fermi level E_F. For one conduction electron per atomic volume v_a

$$k_m=3^{\frac{1}{3}}\pi^{\frac{2}{3}}v_a^{-\frac{1}{3}}, \quad E_F=\hbar^2k_m^2/2m'. \qquad (33)$$

The integration of k' is from k_m to infinity, to include all overlapping higher bands.

There are a few scattering processes with $k\approx k'\approx k_m$, which give a very large contribution, because the energy dominator becomes very small; but these partially cancel. Ruderman and Kittel[6] have shown how the integrations give a finite result:

$$A_{ij}=-2^{-5}(|\Delta_{ij}|^2)_{\mathrm{Av}}m'\pi^{-3}R_{ij}^{-4}\hbar^{-2} \times[\sin(2k_mR_{ij})-2k_mR_{ij}\cos(2k_mR_{ij})]. \qquad (34)$$

Since most of the contribution comes from scattering processes near the Fermi level, $(|\Delta_{ij}|^2)_{\mathrm{Av}}$ in the metal is effectively an average over the Fermi surface.

The main difference between a metal and an insulator is the exponential factor in the latter case. The exponent contains the square root of the energy gap. Whereas the magnitude of the interaction drops off as R_{ij}^{-3} for the metal, like the dipolar interaction, the exponential decrease in the insulator makes the "nearest neighbor only" assumption a good one in this case.

The quantity $|\Delta_{ij}|^2$ calculated from Eqs. (29) and (30) is related to the atomic hyperfine splitting ν^{hfs}:

$$|\Delta_{ij}|^2=\frac{4v_a^2\hbar^2}{(2I_i+1)(2I_j+1)}\nu_i^{\mathrm{hfs}}\nu_j^{\mathrm{hfs}}\xi_i\xi_j, \qquad (35)$$

where $\xi_i=P_i^{\mathrm{eff}}/P_a$ is a numerical factor of the order of unity. P_a is the electron density at the nucleus in the atom in the s-state with hyperfine splitting ν^{hfs}, while P_i^{eff} is the corresponding density in the solid, suitably averaged over valence and conduction bands. For a metal P^{eff} is approximately equal to the density produced at the nucleus, if all electrons were at the Fermi surface, because these electrons give the major contribution in the integral leading to (34). The exchange interaction between a pair of atoms in a metal in the quasi-free electron approximation is proportional to $v_a^2\xi_i^2m'$, whereas the Knight shift is proportional to $v_a\xi_im'$. A different combination of the quantities ξ and the effective mass, or ξ and the density of states, occurs. In principle both $(v_a\xi)$ and m' can therefore be determined. The spin-lattice relaxation gives the same combination of ξ and m', as the Knight shift.

TABLE VI. Sign of the exchange interaction.

	Structure	Nearest neighbor	Next nearest neighbor
Insulator	bcc	−	+
	fcc	−	+
Metal	bcc	+	−
	fcc	+	−

The factor v_a^2 appears in (35) because of the normalization condition (29). Taking $R_{ij}^3\approx v_a$ in (34), it is seen from (33) and (35) that A_{ij} has the order of magnitude of the square of the hyperfine splitting over the Fermi energy.

For insulators the interaction between nearest neighbors will in general be somewhat smaller. The ratio of the exchange with respect to the classical dipolar interaction increases rapidly for heavier isotopes as the effective electron density P^{eff} increases. Kittel estimates that this ratio is unity for silver. It is about 15 for thallium. For a pair of sodium atoms the exchange interaction would be roughly 5 percent of the dipolar interaction, but for a sodium-thallium pair it would again be of the order of unity. These qualitative estimates hold for elements as well as compounds, for molecules as well as coherent matter, for metals as well as insulators. In molecules with a low-lying ground level and in insulators with a large forbidden gap the effects will clearly be smaller, but nuclear spin exchange should always give marked effects, whenever heavy isotopes are present.

The sign of the exchange interaction is determined by the function $-\sin x+x\cos x$ with $x=k_tR_{ij}$ in insulators, and $x=2k_mR_{ij}$ in metals. For a b.c.c. insulator we have $A_{ij}<0$ for nearest neighbors, but $A_{ij}>0$ for next nearest neighbors. Since the nearest neighbor interaction dominates due to the exponential factor, the nuclear magnetic moments will tend to align parallel. Other data for the f.c.c. structure and for metals are compiled in Table VI. It is seen that the nuclear moments in a b.c.c. metal would tend to align in two antiparallel systems. In the case of metals the alignment of the nuclear spins is however also determined in part by the first-order spin interaction with the conduction electron spins, as discussed by Fröhlich.[25] This and the long-range character of the nuclear spin exchange makes a prediction of nuclear spin ordering in metals difficult. The simpler case of insulators allows the prediction that the b.c.c. and f.c.c. lattices of nuclear spins will show a ferromagnetic ordering at very low temperatures. The Curie point of the thallium oxide with $\hbar^{-1}A_{ij}=1.2\times10^4$ cps and $z=12$ would lie at

$$T_c=2zAI(I+1)/3k=3.46\times10^{-6}\ {}^{\circ}\mathrm{K}. \qquad (36)$$

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[25] H. Fröhlich and F. R. N. Nabarro, Proc. Roy. Soc. (London) **175**, 382 (1940).

Its band structure is more complicated than the present treatment allows for. It is only a reasonable guess that it will become nuclear ferromagnetic, but the occurrence of some type of nuclear alignment below this temperature is certain to exist, independent of the shape of the specimen. The moot question of alignment by dipolar interaction alone is not involved.[26]

Unfortunately the relaxation times to establish thermal equilibrium will become prohibitively long in insulators at such low temperatures. Experimentally metals would be more suited for the investigation of nuclear magnetism at extremely low temperatures, but here the theoretical situation is less certain.

Although the simplifications made in obtaining Eqs. (32) and (34) are too crude to allow an actual calculation of A_{ij} even for simpler structures than thallium and thallium oxide, we wish to show that the order of magnitude is in agreement with the experimental values. Using the geometry of a f.c.c. lattice with 12 nearest neighbors at 3.45×10^{-8} cm for both metal and oxide, the known atomic hyperfine splitting[27] in the $6s^2\,7s$ state, $\nu^{\mathrm{hfs}}=0.4$ cm^{-1}, an effective mass equal to the free electron mass, one obtains for the metal $h^{-1}A_{ij}=2.2$ kc/sec. Agreement with experiment is obtained when $\xi=2.8$. The effective electron density must be taken 2.8 as large as in the atomic $6s^2\,7s$ state, or 1.5 times as large as in the $6s^2\,6p\;{}^2P_{\frac{1}{2}}$ state. To obtain the correct Knight shift of 1.56 percent, $\xi=1.64$ should be taken. The discrepancy merely points to the inadequacy of the quasi-free electron model in this case. There is no justification for an attempt to derive a better value for the effective mass.

If one assumes the same effective density and the free electron mass for the oxide, Eq. (32) gives agreement with the experimental value $h^{-1}A_{ij}=12$ kc/sec if the energy gap is taken as $E_g=0.12$ ev. The experimental data and the theoretical expressions can thus be made to agree with reasonable values of the physical constants.

The problem of crystalline anisotropy for which there is no room in the spherical approximation can be discussed in a formal manner by expanding the wave function ψ_{k} and the energy denominator in a series of spherical harmonics consistent with the crystalline symmetry. For a crystal with axial symmetry one could, e.g., write

$$\begin{aligned}\psi_{\mathrm{k}}&=(u_{\mathrm{k}}+ik\alpha_1u_{1\mathrm{k}}\cos\theta_{\mathrm{kc}}+\cdots)e^{i\mathbf{k}\cdot\mathbf{r}}\\ &\times\{E(\mathbf{k}')-E(\mathbf{k})\}^{-1}=E^{-1}+\Delta E_{\mathrm{k}}^{-1}\tfrac{1}{2}(3\cos^2\theta_{\mathrm{kc}}-1)\\ &\qquad+\Delta E_{\mathrm{k}'}^{-1}\tfrac{1}{2}(3\cos^2\theta_{\mathrm{k'c}}-1)+\cdots,\end{aligned}$$

where θ_{kc} is the angle between the wave vector **k** and the crystallographic axis **c**. Repeating the calculation of A_{ij} with the addition of these terms gives upon integration terms depending on the angle between $\mathbf{R}_{ij}$ and **c**. The spin dependence of the interaction still has the scalar product form. The magnitude of the exchange constant will depend somewhat on the orientation of $\mathbf{R}_{ij}$. It will not be possible to observe this effect with the techniques described in this paper. Only the average exchange interaction for a number of neighbors is measured. Therefore no explicit calculation will be presented.

The pseudo-dipolar interaction does not have its origin in crystalline anisotropy, but in the tensor character of the dipolar interaction of the second term in the Hamiltonian (27). The important differences caused by the angular dependence of this interaction must now be considered. The terminology "anisotropic exchange" which has often been used to denote the pseudo-dipolar interaction in papers on electron magnetism has been avoided in the present article. It is clear from this paragraph that its use may be misleading.

VI. THEORY OF PSEUDO-DIPOLAR INTERACTION

It will be convenient to write the angular dependence of all quantities in terms of spherical harmonics $P_l^{|m|}(\cos\theta)$, which are related to the normalized, generalized Laplace spherical functions by

$$Y_l^m=(-1)^m\left[\frac{2l+1}{2}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}\times P_l^{|m|}(\cos\theta)(2\pi)^{-\frac{1}{2}}e^{im\phi}.\qquad(37)$$

When θ_{kr} and ϕ_{kr} correspond to the angle between two vectors **k** and **r**, the shorthand notations ${}^{kr}P_l^m\equiv P_l^m(\cos\theta_{kr})$ and $P_l^{-m}=(-1)^m[(l-m)!/(l+m)!]P_l^m$ are introduced. The orthogonality properties of these functions are well known.[28] Frequent use will be made of the addition theorem,

$${}^{ab}P_l=\sum_{m=-l}^{l}(-1)^m\,{}^{ac}P_l^m\,{}^{bc}P_l^{-m}e^{im(\phi_{\mathrm{ab}}-\phi_{\mathrm{bc}})},\qquad(38)$$

of its immediate consequence,

$$\iint{}^{ab}P_l\,{}^{bc}P_l^m d\Omega_{\mathrm{b}}=\left(\frac{4\pi}{2l+1}\right){}^{ac}P_l^m e^{im\phi_{\mathrm{ac}}},\qquad(39)$$

where $d\Omega_{\mathrm{b}}$ is an element of solid angle of the vector space **b**, and of the expansion formula for a plane wave used in most scattering problems,

$$e^{i\mathbf{k}\cdot\mathbf{r}}=\left(\frac{2}{\pi}kr\right)^{-\frac{1}{2}}\sum_{l=0}^{\infty}(2l+1)i^lJ_{l+\frac{1}{2}}(kr)\,{}^{kr}P_l.\qquad(40)$$

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[26] J. A. Sauer and A. N. V. Temperley, Proc. Roy. Soc. (London) **176**, 203 (1940); J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937); J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946).

[27] P. Brix and H. Kopferman, *Landolt-Bornstein, Zahlenwerte und Funktionen* I 5 (Springer, Berlin, 1952).

[28] See, e.g., F. Sauter, *Differentialgleichungen der Physik* (Sammlung Goschen, Berlin, 1942); P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), pp. 1274 ff; L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), Chap. 5.

The Bessel function of half-integral order $J_{l+\frac{1}{2}}$ can be expressed in the cosine and sine functions and odd powers of $(kr)^{-\frac{1}{2}}$.

Consider the tensor part of the Hamiltonian (27). Since the nuclear spins are quantized with respect to the external field **H**, the dipolar interaction between nuclear spin $\mathbf{I}_i$ and electron spin **S** can conveniently be expanded[29] in harmonics containing the angle between $\mathbf{r}_i$ and **H**,

$$\begin{aligned}\mathcal{H}_{\text{tensor}}=gg_N\beta\beta_N r_i^{-3}\big[&(-2I_zS_z+\tfrac{1}{2}I_+S_-+\tfrac{1}{2}I_-S_+)\ {}^{Hr_i}P_2\\&-\tfrac{1}{2}(I_+S_z+I_zS_+)\ {}^{Hr_i}P_2{}'e^{-i\phi_{Hr}}-\tfrac{1}{2}(I_-S_z+I_zS_-)\\&\times{}^{Hr_i}P_2{}^1e^{+i\phi_{Hr}}-\tfrac{1}{4}I_+S_+\ {}^{Hr_i}P_2{}^2e^{-2i\phi_{Hr}}\\&-\tfrac{1}{4}I_-S_-\ {}^{Hr_i}P_2{}^2e^{-2i\phi_{Hr}}\big].\end{aligned}\qquad(41)$$

$g=2.0023$ is the electron spin gyromagnetic ratio. I_z and S_z are the components of spin parallel to the magnetic field H; S_+, S_-, I_+, I_- are the usual spin raising and lowering operators.

Bardeen[30] and others[31] have shown that the periodic function $u_k(\mathbf{r})$ in the Bloch wave function (26) can be expanded in a fairly rapidly converging power series in **k**, in the spherical approximation. This is automatically an expansion in spherical harmonics:

$$\begin{aligned}u_k(\mathbf{r})={}^0u_k(r)+ikc_1\,{}^1u_k(r)\ {}^{kr}P_1\\-k^2c_2\,{}^2u(r)\ {}^{kr}P_2+\cdots.\end{aligned}\qquad(42)$$

The coefficients c_1 and c_2 are constant near the origin $k=0$, the bottom of the band. Brooks[31] has shown how they may be determined from the boundary conditions of the lowest wave function on the Wigner-Seitz sphere.

Consider the second-order interaction between nuclear spins i and j, whereby an electron is excited from the initial state with wave vector **k** and spin orientation **s** to the intermediate state with **k′** and **s′** by the first term in the tensor interaction (41) of nuclear spin i, and back from the intermediate state to the ground state by the scalar interaction of spin j:

$$\begin{aligned}\frac{16\pi}{3}&gg_{Ni}g_{Nj}\beta^2\beta_N{}^2(s|-2I_{iz}S_z+\tfrac{1}{2}I_{i+}S_-+\tfrac{1}{2}I_{i-}S_+|s')\\&\times(s'|I_{jz}S_z+\tfrac{1}{2}I_{j+}S_-+\tfrac{1}{2}I_jS_+|s)\{E(\mathbf{k}')-E(\mathbf{k})\}^{-1}\\&\times e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_i}\int_0^{r_s}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i}u_{k'}{}^*r_i^{-3}\ {}^{Hr}P_2u_kr_i^2dr_id\Omega_{r_i}\\&\times e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_j}u_{k'}{}^*(\mathbf{R}_j)u_k(\mathbf{R}_j).\end{aligned}\qquad(43)$$

s and s' are the spin quantum numbers in the ground state and the excited state. The integration over $\mathbf{r}_i$ is extended only over the Wigner-Seitz sphere with radius $r_s=[(3/4\pi)\surd a]^{\frac{1}{3}}$ around the ith nucleus. The dipolar interaction drops off as r_i^{-3} and the small contribution from values $r_i>r_s$ is neglected. Furthermore exp $[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i]$ is replaced by unity inside the sphere. Actually $(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_s$ may not be a small quantity. There is no selection rule on **k** in the transition as the perturbation is localized. As far as nuclear spin orientation is concerned the lattice is not periodic. Exp $[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]$ might be expanded with the aid of (40), and the radial and angular dependence on $\mathbf{r}_i$ could still be separated; but in order to keep the integrations relatively simple the exponent is replaced by unity.[32] Substitute for u_k and $u_{k'}$ the expansion (42). Introduce the abbreviations

$$\begin{aligned}{}^{sd'}\Delta_i(kk')&={}^{sd'}\Delta_i^*(k'k)\\&=gg_{Ni}\beta\beta_N\int_0^{r_s}{}^2u_k{}'^*(r_i)\ {}^0u_k(r_i)r_i^{-1}\,dr_i,\end{aligned}\qquad(44\text{a})$$

$$\begin{aligned}{}^{s'd}\Delta_i(kk')&={}^{s'd}\Delta_i^*(k'k)\\&=gg_{Ni}\beta\beta_N\int_0^{r_s}{}^0u_k{}'^*(r_i)\ {}^2u_k(r_i)r_i^{-1}\,dr_i,\end{aligned}\qquad(44\text{b})$$

$$\begin{aligned}{}^{pp'}\Delta_i(kk')&={}^{pp'}\Delta_i^*(k'k)\\&=gg_{Ni}\beta\beta_N\int_0^{r_s}{}^1u_k{}^*(r_i)\ {}^1u_k(r_i)r_i^{-1}\,dr_i.\end{aligned}\qquad(44\text{c})$$

Usually the radial functions in (42) are real. Henceforth the Δ's will be written as real quantities, to simplify notation, although the calculation could easily be carried through for complex quantities. Use Eq. (39) and the relation

$$\int{}^{kr_i}P_1\ {}^{k'r_i}P_1\ {}^{Hr_i}P_2\,d\Omega_{r_i}=\frac{8\pi}{15}(-\,{}^{kk'}P_1+3\ {}^{Hk}P_1\ {}^{Hk'}P_1)$$

to evaluate the integral over the solid angle $d\Omega_{r_i}$. Carry out the summation over the two electron spin orientations in the initial and intermediate states. The second-order interaction (43) then takes the form

$$\begin{aligned}+\tfrac{1}{2}&(-2I_{iz}I_{jz}+\tfrac{1}{2}I_{i+}I_{j-}+\tfrac{1}{2}I_{i-}I_{j+})[E(k')-E(k)]^{-1}\\&\times e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}}\Delta_j(k',k)\bigg[-\frac{4\pi}{5}c_2{}'k'^2\ {}^{sd'}\Delta_i(k,k')\ {}^{Hk'}P_2\\&-\frac{4\pi}{5}c_2k^2\ {}^{s'd}\Delta_i(k,k')\ {}^{Hk}P_2+\frac{8\pi}{15}c_1{}'c_1k'k\ {}^{pp'}\Delta_i(k,k')\\&\times\{3\ {}^{Hk}P_1\ {}^{Hk'}P_1-{}^{kk'}P_1)\}\bigg].\end{aligned}\qquad(45)$$

Two permutations of this interaction must be made. The tensor interaction (41) may act on the nuclear spin j and the scalar interaction on i, and the inter-

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[29] M. H. Cohen, Phys. Rev. **95**, 674 (1954).

[30] J. Bardeen, J. Chem. Phys. **6**, 367 (1937).

[31] W. Kohn, Phys. Rev. **87**, 472 (1952); H. Brooks, Phys. Rev. **91**, 1027 (1953).

[32] For quantitative work this simplification is not permissible. The exponential factors will in many cases give the larger contribution to the angular dependence.

mediate state may be excited by the interaction with spin j, while the return to the ground state is made through the interaction with spin i. The last permutation will result in the addition of the complex conjugate expression. Finally one has to sum over all occupied states $\mathbf{k}$ and all unoccupied states $\mathbf{k}'$. This integration over $\mathbf{k}$ and $\mathbf{k}'$-space will be carried out by separating again the angular and radial dependence.

Assume that the quantities Δ, given by (29) and (44), and $[E(\mathbf{k}')-E(\mathbf{k})]^{-1}$ do not depend on the direction of $\mathbf{k}$ or $\mathbf{k}'$. The changes which result when this restriction is not made, will be discussed later. The angular integrations over $d\Omega_k$ and $d\Omega_{k'}$ can then be completed, when $\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}]$ in (45) is expanded according to (40). The interaction between the nuclear spins becomes

$$(-2I_{iz}I_{jz}+\tfrac{1}{2}I_{i+}I_{j-}+\tfrac{1}{2}I_{i-}I_{j+})\,{}^{HR_{ij}}P_2B_{ij},$$

with

$$\begin{aligned}
B_{ij}&=\int_k\int_{k'}(b_1+b_2+b_3)[E(k')-E(k)]^{-1}\\
&\qquad\times(2\pi)^{-6}k^2k'^2dkdk',\\
b_1(k,k')&=\frac{128\pi^4}{15}c_1c_1'kk'(\Delta_j{}^{pp'}\Delta_i+{}^{pp'}\Delta_j\Delta_i)_{kk'}\\
&\qquad\times(kk'R_{ij}^2)^{-\frac{1}{2}}J_{\frac{3}{2}}(kR_{ij})\,J_{\frac{3}{2}}(k'R_{ij}),\qquad(46)\\
b_2(k,k')&=\frac{32\pi^4}{5}c_2k^2(\Delta_j{}^{s'd}\Delta_i+\Delta_i{}^{s'd}\Delta_j)_{kk'}\\
&\qquad\times(kk'R_{ij}^2)^{-\frac{1}{2}}J_{\frac{5}{2}}(kR_{ij})\,J_{\frac{1}{2}}(k'R_{ij}),\\
b_3(k,k')&=\frac{32\pi^4}{5}c_2'k'^2(\Delta_j{}^{sd'}\Delta_i+\Delta_i{}^{sd'}\Delta_j)_{kk'}\\
&\qquad\times(kk'R_{ij}^2)^{-\frac{1}{2}}J_{\frac{1}{2}}(kR_{ij})\,J_{\frac{5}{2}}(k'R_{ij}).
\end{aligned}$$

Repeat the same calculation for the other terms of the tensor interaction (41), using (39). As an immediate consequence of group-theoretical arguments, the final result for the pseudo-dipolar interaction is

$$\mathcal{H}_{ij}{}^{\mathrm{dip}}=\{\mathbf{I}_i\cdot\mathbf{I}_j-3R_{ij}^{-2}(\mathbf{I}_i\cdot\mathbf{R}_{ij})(\mathbf{I}_j\cdot\mathbf{R}_{ij})\}B_{ij}.\qquad(47)$$

As before the slight dependence of $E(k)-E(k')$ on the spin orientations has been neglected in this derivation, consistent with the spherical approximation. Spin-spin and spin-lattice relaxation processes can be defined for the pseudo-dipolar interaction in exactly the same manner as for the classical dipolar interaction.

The constant B_{ij}, which was introduced earlier in a phenomenological fashion, is now expressed quite generally by Eq. (46). The integration over the wave numbers can be carried out with certain simplifying assumptions, which may be adapted to the particular type of solid under investigation. The same assumptions will be made as in the discussion of the ordinary exchange interaction.

Assume that an insulator has a narrow valence band and a relatively wide gap E_g. Replace all higher bands by one conduction band with one effective mass m'. Then Eq. (30) may be used. Introduce suitable averages for the products of Δ's quantities, appearing in the expressions for b_1, b_2 and b_3. These are analogous to the quantity $|\Delta_{ij}|_{\mathrm{Av}}{}^2$ introduced in (29a). They are related to the atomic hyperfine structure in the corresponding p-state by an expression similar to (35). The p-type hyperfine interaction in the solid has the order of magnitude of the atomic p-type hyperfine splitting times the percentage of p-type character (or $s-d$ mixture) of the solid state wave function. Integrate k from 0 to k_t, the top of the valence band, given by (31) and k' from 0 to infinity. The integral (46) appears to diverge at the latter limit. The reason is that the coefficients c in the expansion certainly cannot remain constant to $k\rightarrow\infty$. Physical reality requires a normalization. Assume $c_1'=c_1'(1+ak'^2)^{-1}$ and $c_2'=c_1'\times(1+bk'^4)^{-1}$ as $k'\rightarrow\infty$, or some such relations, to insure convergence. The integration over k' can be carried through in the complex plane. In the result let $a\rightarrow 0$ and $b\rightarrow 0$. The parabolic law $E=\hbar k'^2/2m'$ is assumed in the band region of interest. The integration over k is elementary:

$$\begin{aligned}
{}^{\mathrm{ins}}B_{ij}&=\pi^{-2}\hbar^{-2}m'R_{ij}^{-6}\exp\{-\hbar^{-1}(2mE_g)^{\frac{1}{2}}R_{ij}\}\\
&\times\Bigg[\frac{4}{15}c_1c_1'\langle\Delta_i{}^{pp'}\Delta_j+{}^{pp'}\Delta_i\Delta_j\rangle_{\mathrm{eff}}\,(1+\hbar^{-1}(2mE_g)^{\frac{1}{2}}R_{ij})\\
&\times\int_0^{k_tR_{ij}}(\sin x-x\cos x)x\,dx+\frac{1}{15}c_2\langle\Delta_i{}^{s'd}\Delta_j+{}^{s'd}\Delta_i\Delta_j\rangle_{\mathrm{eff}}\\
&\times\int_0^{k_tR_{ij}}\{(3-x^2)\sin x-3x\cos x\}x\,dx\\
&+\frac{1}{15}c_2'\langle\Delta_i{}^{sd'}\Delta_j+{}^{sd'}\Delta_i\Delta_j\rangle_{\mathrm{eff}}(3+3\hbar^{-1}(2mE_g)^{\frac{1}{2}}R_{ij}\\
&\qquad+2\hbar^{-2}mE_gR_{ij}^2)\int_0^{k_tR_{ij}}x\sin x\,dx\Bigg].\qquad(48)
\end{aligned}$$

Comparison of this result with Eq. (32) shows that the pseudo-dipolar interaction has a radial dependence similar to that of the isotropic exchange, since the integrals go as R_{ij}^3 for large R_{ij}. At large distances the exponential factor is however dominating. The ratio $B_{ij}A_{ij}^{-1}$ has the order of magnitude of the hyperfine splitting ratio in corresponding p- and s-states times the relative amount of p- with respect to s-character of the wave function. Rather large variations around this order of magnitude can occur because of the different trigonometric functions in (32) and (48). Accidentally these could even make one of the quantities A_{ij} or B_{ij} zero, the other remaining finite.

A similar state of affairs for the ratio B_{ij}/A_{ij} occurs in metals. In this case k in Eq. (46) must be integrated from 0 to k_m, and k' from k_m to infinity over the conduction band. The integration of k' can formally be changed from zero to infinity without changing the result. The integrand is antisymmetric in k and k' and consequently

$$\int_0^{k_m}\int_0^{k_m}(b_1+b_2+b_3)[E(k')-E(k)]^{-1}\times(2\pi)^{-6}k^2k'^2dkdk'=0.$$

If one takes $E(k')-E(k)=(2m)^{-1}\hbar^2(k'^2-k^2)$, the principal value of the integral over k' can be evaluated in the complex plane.

$$\begin{aligned}{}^{\text{met}}B_{ij}=\pi^{-2}\hbar^{-2}m_{\text{eff}}R_{ij}^{-6}\Bigg[&\frac{4}{15}c_1c_1'\langle\Delta_i\,{}^{pp'}\Delta_j+{}^{pp'}\Delta_i\Delta_j\rangle_{\text{Fermi}}\\&\times\int_0^{k_mR_{ij}}(\sin x-x\cos x)(\cos x-x\sin x)xdx\\&+\frac{1}{15}c_2\langle\Delta_i\,{}^{s'd}\Delta_j+{}^{s'd}\Delta_i\Delta_j\rangle_{\text{Fermi}}\int_0^{k_mR_{ij}}\cos x\\&\times\{(-x^2+3)\sin x-3x\cos x\}xdx\\&+\frac{1}{15}c_2'\langle\Delta_i\,{}^{sd'}\Delta_j+{}^{sd'}\Delta_i\Delta_j\rangle_{\text{Fermi}}\\&\times\int_0^{k_mR_{ij}}\sin x\{(-x^2+3)\cos x+3x\sin x\}xdx\Bigg].\end{aligned}\tag{49}$$

The integrations over $x=kR_{ij}$ are elementary and can be carried through by repeated partial integrations. The integrals go as R_{ij}^3 for large R_{ij}. The pseudo-dipolar interaction therefore has a R_{ij}^{-3} dependence in metals. The ratio B_{ij}/A_{ij} in the metal has again the order of magnitude of the ratio of the hyperfine splitting is pure p- and s-states multiplied by the relative amount of p- and s-character, respectively. The effective average of the products of the quantities Δ is now approximately equal to the value of this product on the Fermi surface, since electron scattering processes between k-states close to this surface contribute most to the integrals. At the Fermi surface the relative amount of p-character of the wave function may frequently exceed the amount of s-character. Taking the hyperfine splitting in a pure p-state to be about 10 percent of that in an s-state, B_{ij}/A_{ij} can still easily assume a value of, say, 30 percent. This is particularly true if the variations in the numerical values of the trigonometric expressions involved in A_{ij} and B_{ij} are taken into account. The observed ratio $B_{ij}/A_{ij}=0.3$ for nearest neighbors in thallium is thus entirely reasonable. It indicates that the amount p-character probably exceeds the amount of s-character of the electron wave functions at the Fermi-surface in this metal. Quantitative conclusions are difficult to make, as Eqs. (34) and (49) are rather crude approximations for this case. The complicated band structure would certainly make a numerical evaluation of integrals (46) necessary.

Resonance lines in pure isotopes will in general not have widths narrower than the classical dipolar interaction due to exchange narrowing. Usually the pseudo-dipolar interaction will be a sizeable fraction of the exchange interaction, and the lines will be rather broader than Van Vleck's formula for classical dipolar interaction would predict.

The fact that the Pb^{207} resonance in natural lead is rather broad, while Pb^{207} with 22.6 percent abundance is the only stable lead isotope with nonzero spin, indicates pseudo-dipolar interaction in metallic lead. To estimate the magnitude of both the exchange and pseudo-dipolar interaction in this case, measurements on the Pb^{207} in the presence of another isotope with nonzero spin should be made. The rapid increase in line width on alloying observed[1] in some cases may be due in part to exchange broadening.

The pseudo-dipolar interaction has the same order of magnitude in cubic crystals as in noncubic crystals. One could formally add to the expansion (42) terms depending on the angle between $\mathbf{r}$ and the crystallographic axes. For an axially symmetric crystal the leading term in the expansion for the wave function would be $ik\sigma_1\,{}^{rc}P_1$ and in the energy ${}^{rc}P_2$, where $\mathbf{c}$ is the unit vector in the direction of the axis of symmetry. In angular integration small terms are added to the result. One effect is that the constant B_{ij} may depend on the angle between $\mathbf{R}_{ij}$ and $\mathbf{c}$. The changes are not observable in the experiments described in this paper.

Finally the second-order perturbation with the tensor interaction (42) on both nuclei i and j must be considered. Two integrals over $\mathbf{r}_i$ and $\mathbf{r}_j$, containing ${}^{Hr_i}P_2^m$ and ${}^{Hr_j}P_2^m$ will now occur, instead of the single one over $\mathbf{r}_i$ in Eq. (43). The interaction is still linear in the nuclear spins i and j. From group-theoretical arguments it is clear therefore, that the final dependence on $\mathbf{H}$ contains no spherical harmonics of order higher than the second. Detailed calculations, carrying out the proper summations over the electron spin orientations and going through similar steps which led to Eq. (46) for the tensor-scalar interaction, confirm this. A typical term of the tensor-tensor interaction has the form:

$$\begin{aligned}&-\mathbf{I}_i\cdot\mathbf{I}_j\int_k\int_{k'}(4\pi)^2\left(\frac{4\pi}{5}\right)^2 2c_2^2\,{}^{s'd}\Delta_j(k',k)\,{}^{s'd}\Delta_i(k,k')\\&\times\frac{\pi J_{\frac{1}{2}}(kR)J_{\frac{1}{2}}(k'R)(2\pi)^{-6}}{2(kR_{ij}k'R_{ij})^{\frac{1}{2}}[E(k')-E(k)]}k^6k'^2dkdk'\\&-[\mathbf{I}_i\cdot\mathbf{I}_j-3R_{ij}^{-2}(\mathbf{I}_i\cdot\mathbf{R}_{ij})(\mathbf{I}_j\cdot\mathbf{R}_{ij})]\\&\times\int_k\int_{k'}(4\pi)^2\left(\frac{4\pi}{5}\right)^2 c_2^2\,{}^{s'd}\Delta_j(k',k)\,{}^{s'd}\Delta_i(k,k')\\&\times\frac{\pi J_{\frac{5}{2}}(kR)J_{\frac{1}{2}}(k'R)}{2(kk'R_{ij}^2)^{\frac{1}{2}}[E(k')-E(k)]}(2\pi)^{-6}k^6k'^2dkdk'.\end{aligned}$$

The double tensor-interaction contributes both to the isotropic exchange and the pseudo-dipolar interaction.

There are five additional terms containing different product combinations of ${}^{s'd}\Delta$, ${}^{sd'}\Delta$, and ${}^{pp'}\Delta$. These contributions should be added algebraically to the expressions for A_{ij} and B_{ij} derived previously. The additions have the magnitude of $B_{ij}^2 A_{ij}^{-1}$. The relative correction for A_{ij} in the case of thallium is only 10 percent. Rather wide variations in the actual values of the corrections are possible due to the trigonometric functions. For nearest neighbors the magnitude of the tensor-tensor interaction is the square of hyperfine splitting in the p-state times the square of the fractional amount of p-character, divided by the Fermi energy.

VII. CONCLUDING REMARKS

For a heavy metal with a simple band structure it might be possible to give a quantitative interpretation of observed exchange interactions. The theory is not sufficiently refined to predict the numerical values found for thallium and thallium oxide, although it certainly gives the right order of magnitude. This is already a great deal better than can be achieved for electron spin exchange. Whereas a quantitative atomic theory of ferromagnetic properties is still lacking, nuclear ferromagnetic characteristics may be derived from first principles. This is at least true for insulators, where the exchange interaction is confined to near neighbors and complications with conduction electron spins are avoided. The Curie or Néel temperature is determined by the value A_{ij}, Eqs. (32) and (36).

The dipolar terms will give rise to magnetic anisotropy below the Curie point. Van Vleck's theory for ferromagnetic anisotropy[33] applies equally well to the nuclear case.[34] For cubic spin systems it is necessary to go to higher-order terms in the expansion of the free energy of the nuclear spin system to obtain anisotropy from the dipolar interaction. In such cubic crystals the magnetic anisotropy would then be inversely proportional to the external field H. In ordinary electron ferromagnetism the anisotropy is not field dependent, because the internal Weiss field is always large compared to H. A first-order field-independent anisotropy of nuclear magnetism in cubic crystals may arise from quadrupole-quadrupole coupling, if the nuclear spins have $I>\frac{1}{2}$.

In our opinion, however, the main interest of nuclear spin exchange does not lie in the field of extremely low temperatures and nuclear ferromagnetism. It seems more important that the exchange and pseudo-dipolar interaction give information about the electron wave functions in the lattice and, in particular, about their nonspherical character.

The interaction (27) does not represent the complete Hamiltonian[35] for the nuclear spin I. If the nucleus has a quadrupole moment it will interact with a noncubic charge distribution of the electron which will have matrix elements connecting the ground state $\mathbf{k}$ with the intermediate excited state $\mathbf{k}'$. In second-order perturbation dipole-quadrupole and quadrupole-quadrupole interactions will result. The latter is quadratic in the nuclear spins $\mathbf{I}_i$ and $\mathbf{I}_j$ and has the order of magnitude of the square of the quadrupole hyperfine splitting over the Fermi energy. Since the quadrupole interaction usually produces relatively small deviations from the interval rule, and can only operate on the "non s" character of the wave functions its order of magnitude will in general be even smaller than the tensor-tensor interaction discussed in the preceding section. Since the thallium isotopes have $I=\frac{1}{2}$, the interaction is absent in our experiments and will not be discussed further.

Another term which has not been considered is the nuclear spin-electron orbit interaction $2g_N\beta_N\beta r_i^{-3}\mathbf{I}_i\cdot\mathbf{L}$. It can be safely assumed that the second-order coupling between nuclear spins in solids due to this term is orders of magnitude smaller than the interaction via electron spins, as has been shown to be the case for molecules.[4,5] One can also introduce the electron spin-orbit coupling and consider the interplay of spin and orbital effects. To obtain a nonvanishing result for the nuclear spin interaction, the operators $\mathbf{L}$ and $\mathbf{S}$ should in general each occur in even powers in the Hamiltonian. The orbital effects will not be discussed in this paper. Although they make only a minor contribution to the nuclear spin-spin coupling, they are of great importance for the chemical shifts in solids. The large value of this shift in thallium oxide points to a small energy gap between bands, as did the large value of the exchange constant. It follows from Ramsey's theory[36] that the relative anisotropy of the chemical shift should have the same order of magnitude as the anisotropy in the diamagnetic susceptibility, although they need not have the same value. A relative anisotropy in the chemical shift of 34 percent is thus entirely reasonable. It would be desirable to develop a quantitative theory of the orbital effects in solids on nuclear spins.

A few words must be said about the effect of nuclear motion on the exchange interaction. The influence of diffusion or other types of motion in the nonrigid lattice and in liquids on the pseudo-dipolar interaction is exactly the same as on the classical dipolar interaction, which has been treated in great detail.[37]

The exchange broadening between unlike spins can undergo a motional narrowing too. A pure rotation, leaving the internuclear distance between the two nuclei unchanged, has however no effect in this case.

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The exchange interaction has no angular dependence. Unlike the dipolar interaction, it does not average out on rotation and this is the reason that exchange between unlike neighbors in molecules is observable in liquid and gaseous samples. If the nuclei with their spins diffuse rapidly with respect to each other, the exchange interaction A_{ij} [Eqs. (32) and (34)] has to be averaged over all $\mathbf{R}_{ij}$ and then summed over all j. Another way of describing this same phenomenon is to say that a neighboring position of nucleus i is at one time occupied by a nuclear spin j pointing up and some time later by another spin k pointing down. A complete analysis of this motional narrowing of exchange broadening is beyond the scope of this paper. It is somewhat unexpected that the resonance in liquid metallic thallium could not be observed and the Hg^{199} resonance in liquid mercury is very broad. The thallium resonance in liquid thallium-mercury alloys is also extremely broad. These facts seem to indicate molecular association in the liquid metals. In the rapidly rotating and diffusing molecules the exchange interaction is not averaged, and the interchange of nuclei between molecular assemblies which would lead to narrowing is too slow. A more careful investigation must be made before definite conclusions can be drawn.

Finally the universal character of the exchange coupling between nuclear spins is stressed. It should be considered whenever heavy atoms are involved, not only in metals, but also in valence and ionic crystals as well as in liquids and molecules. In particular, it will make a contribution to splittings observed in molecular spectra with the molecular beam method. A large spin-rotation interaction has been found[38] in the TlCl molecule. It follows from a theoretical analysis of the TlCl molecule in the "very weak field" case[39] that an interaction of the type $A\mathbf{I}_{\mathrm{Cl}}\cdot\mathbf{I}_{\mathrm{Tl}}$, which was not considered, will give rise to a similar splitting of the energy levels, for which $F_1=I_{\mathrm{Cl}}+J$, J, I_{Cl} and I_{Tl} are good quantum numbers, as the considered interaction $C_2\mathbf{I}_{\mathrm{Tl}}\cdot\mathbf{J}$. In principle both interactions contribute to the observed fine structure of the $F=F_1+I_{\mathrm{Tl}}$ levels, and the observed quantity of 73 kc/sec corresponds to C_2-A, and not to C_2 alone. It can be shown, however, that the contribution from A must be small in this case. A distinction between the two types of interaction can be made by changing the isotopic species, since A is proportional to the gyromagnetic ratio of the chlorine isotopes, whereas C_2 is not. The g_N-factors of the chlorine isotopes have the ratio 0.8324, whereas the observed splittings for the $TlCl^{31}$ and $TlCl^{33}$ molecules were the same within a 3 percent accuracy. Similarly the pairs $Rb^{85}F$ and $Rb^{87}F$ have roughly the same splitting,[40] although the g-factors for the Rb isotopes differ by more than a factor three. Only when two heavy isotopic species are present in the diatomic molecule a contribution of A of 10 kc/sec or more can be expected and the nuclear spin exchange might become observable in molecular beam experiments.

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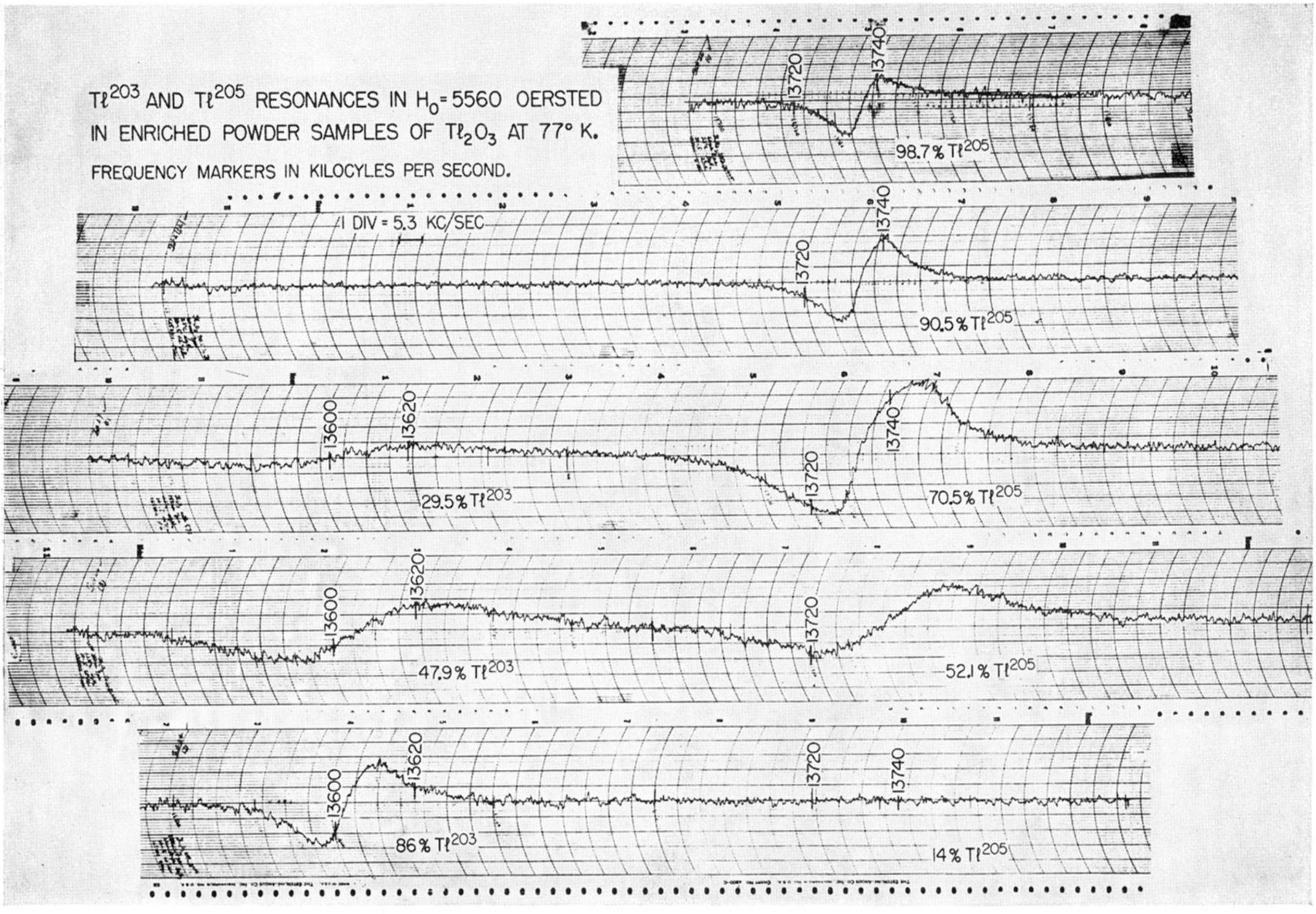

FIG. 1. Experimental recordings of the derivative of the nuclear magnetic resonance absorption in Tl_2O_3 for various isotopic compositions.