

Ultrasonic Investigation of Nuclear Spin-Lattice Relaxation.

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(ricevuto il 17 Dicembre 1958)

CONTENTS. — 1. Introduction. — 2. Theory. — 3. Experimental technique.
— 4. Results and discussion.

1. — Introduction.

Ultrasonics has been utilised extensively in the past to study the properties of gases and liquids which threw light on many molecular processes and has proved to be a very convenient tool in the study of relaxation phenomena. In solids it has been used very effectively in studying the elastic constants from velocity measurements, especially in single crystals. From damping and attenuation measurements there have been attempts to seek information regarding imperfections- dislocations and radiation damage and their kinetics. Recently Ultrasonics has proved to be very helpful in studying the properties of conduction electrons in metals, especially when the metal becomes superconducting ⁽¹⁾. The number of thermally excited electrons can be determined from the measurements of ultrasonic absorption in superconductors. As a matter of fact, MORSE and BOHM ⁽²⁾ claim to have measured the energy gap in the electron energy spectrum in superconducting tin and indium, which, however, has been questioned by some workers ⁽³⁾. Ultra-

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sonic waves have been shown to induce transitions ^(4,5) in the spin energy levels of a particular nucleus through the nuclear spin-lattice relaxation, the possibility of which was suggested first of all by ALTSCHULER ⁽⁶⁾. The possibility of a strong interaction between ultrasonic waves and spin waves, especially when both the magnon and phonon frequencies and wavelengths are equal, has been discussed in ferromagnetic crystals and shown to provide an independent measure of the exchange energy constant ⁽⁷⁾. The potentialities of Ultrasonics in the Gigahertz region, where the acoustic frequencies have wavelengths comparable to the wavelength of light and the phonon energy may approach thermal energy at liquid helium temperatures, are many but its application is, however, limited by the inherent experimental difficulties. The highest frequency which has been achieved as reported recently by BARANSKII ⁽⁸⁾, and BOMMEL and DRANSFELD ⁽⁹⁾ is only 2.5 GHz ^(*).

In many solids nuclear spin lattice relaxation is known to involve the presence of impurities. It has been shown by ROLLIN and HATTON ^(10,11) and by BLOEMBERGEN ⁽¹²⁾ that for nuclei with a spin $I = \frac{1}{2}$, which have no quadrupole moments, the observed spin-lattice relaxation times can be satisfactorily accounted for by assuming that they are due to the presence of electronically paramagnetic impurities. However, for nuclei with a spin $I > \frac{1}{2}$, POUND ⁽¹³⁾ has obtained strong evidence that in pure crystals at not too low temperatures the quadrupolar relaxation may be more important than the impurity relaxation. KRANENDONK ⁽¹⁴⁾ has developed a method for calculating the relaxation time due to the perturbation of this quadrupolar interaction by the lattice vibrations. The interaction between atomic nuclei and their surroundings can be studied by nuclear paramagnetic resonance ⁽¹⁵⁾ or nuclear induction ⁽¹⁶⁾. Such interactions affect relaxation times ^(17,18), line widths ^(17,19) and frequen-

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^(*) Note added in proof. - Recently JACOBSEN has extended the frequency to the vicinity of 10 GHz (*Phys. Rev. Lett.*, **2**, 249 (1959)).

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cies^(20,21). Excitation of ultrasonic vibrations in a crystal offers another method to study the strength and nature of the coupling between lattice vibrations and the nuclear quadrupole moment. Ultrasonic waves can induce nuclear spin transition in solids through the interaction of the quadrupole moment of the nucleus, with the electric field gradient at the site of the nucleus, which varies periodically with the frequency of sound waves.

2. - Theory.

The electrostatic interaction energy \mathcal{H} of a nucleus with the charges constituting its environment is given by

$$(1) \quad \mathcal{H} = \int \rho(x) V(x) d^3x,$$

where the integration is taken over the nuclear volume, $\rho(x)$ is the nuclear charge density and $V(x)$, the electrostatic potential arising from all charges other than those of the nucleus under consideration. Expanding the potential $V(x)$ in a power series about the nuclear center of mass, we obtain

$$\begin{aligned} \mathcal{H} &= \int d^3x \rho(x) \left\{ V_0 + \sum_j \left(\frac{\partial V}{\partial x_j} \right)_0 x_j + \frac{1}{2} \sum_{j,k} \left(\frac{\partial^2 V}{\partial x_j \partial x_k} \right) x_j x_k + \dots \right\} = \\ &= ZeV_0 + \sum_j P_j \left(\frac{\partial V}{\partial x_j} \right)_0 + \frac{1}{2} \sum_{j,k} Q_{jk} \left(\frac{\partial^2 V}{\partial x_j \partial x_k} \right)_0 + \dots, \end{aligned}$$

where

$$\begin{aligned} \int d^3x \rho(x) &= Ze = \text{nuclear charge}, \\ \int d^3x \rho(x) x_j &= P_j = \text{electric dipole moment}, \\ \int d^3x \rho(x) x_j x_k &= Q_{jk} = \text{electric quadrupole moment tensor}. \end{aligned}$$

The first term represents the electrostatic energy of a point nucleus, which is independent of nuclear size, shape or orientation and is of no interest to us. The second term which arises due to electric dipole moment vanishes by virtue of the fact that the nuclear ground state is non-degenerate and the time

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averaged charge distribution satisfies the symmetry condition $\varrho(x) = \varrho(-x)$.

Leaving all other non-vanishing terms in the series except the quadrupole terms, the interaction energy is represented by

$$(3) \quad \mathcal{H} = \frac{1}{2} \sum_{j,k} Q_{jk} V_{jk},$$

where $V_{jk} = (\partial^2 V / \partial x_j \partial x_k)$ and Q_{jk} and V_{jk} are second rank symmetric tensors. V_{jk} , however, can be expressed as $V_{jk} = -\partial E_k / \partial x_j$, where $E_k = -\partial V / \partial x_k$ is the electric field at the nucleus. Thus V_{jk} represents the gradient of the electric field and interacts with the nuclear electric quadrupole moment.

However, in order to have correct evaluation of the interaction energy, one has to consider the polarization of the charge cloud surrounding the nucleus by nuclear quadrupole moment, which has been discussed in detail by STERNHEIMER and his associates⁽²²⁻²⁴⁾. The induced quadrupole moment can be much larger than the nuclear quadrupole moment and is such as to reinforce the nuclear quadrupole moment. This is called antishielding or polarization effect. FOLEY, STERNHEIMER and TYCKO⁽²⁵⁾ find that in ions such as Cl^- , Cu^+ , Rb^+ and Cs^+ the induced quadrupole moment is 10 to 100 times larger than the coupling obtained when there is no polarization effect. KRANENDONK has taken this effect into consideration by means of a multiplication factor

$$(4) \quad \mathcal{H}' = \alpha \mathcal{H} = \alpha \int \varrho(x) V(x) d^3x,$$

where \mathcal{H}' is the interaction energy when polarization of the atomic core is taken into consideration. There is another effect which is also present. The direct field from the surrounding charges polarizes the central ion and leads to an extra field in a direction opposite to the direct field. It is called the shielding effect and its effect on the quadrupolar spin-lattice relaxation is small.

KRANENDONK also drew attention to the effects of covalency which have been discussed in detail by YOSIDA and MORIYA⁽²⁶⁾. If the lattice is deformed by the lattice vibrations, mixing of p - or d -like orbitals into the s -like wavefunctions of ions takes place and as a result the electrons in these non-spherically symmetric orbitals give rise to an electric field gradient at the nucleus which interacts with nuclear quadrupole moments. The resulting quadrupole

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spin-lattice coupling can be much larger than with the direct field alone. As a matter of fact YOSIDA and MORIYA have shown that the relaxation time due to covalency is shorter by a factor of 10^{-4} than in the pure ionic case.

A detailed theory of quadrupolar nuclear spin-lattice relaxation has been formulated by KRANENDONK for crystals of the NaCl-type. He considered one parameter model where the nearest neighbours of a given nucleus are replaced with point charges of magnitude $q = \gamma e$. The magnitude q of these charges is the only adjustable parameter of this model. The dimensionless quantity γ is a measure of the strength of the spin-lattice coupling and e is the electronic charge. Values of γ are obtained by comparing the experimental values of the relaxation time with the values calculated on the basis of the point charge model. For example, in ionic crystals of the NaCl-type spin lattice coupling is due to interaction of the nuclear quadrupole moment with the electric field arising from six equal point charges on the six neighbouring lattice sites and the rest of the charges are supposed to be absent from the crystal. According to his calculations, values of γ are of the order $10^2 \div 10^3$.

KRANENDONK expressed the interaction Hamiltonian as

$$(5) \quad \mathcal{H}' = \sum_{\mu} W_{\mu} Q_{\mu},$$

where Q_{μ} are the components of the nuclear quadrupole moment, the equivalent operators of which in the subspace $I = \text{constant}$ are given by

$$(6) \quad \begin{cases} Q_0 = C[3I_z^2 - I(I+1)], \\ Q_{\pm 1} = C[I_z(I_x \pm iI_y) + (I_x \pm iI_y)I_z]/2, \\ Q_{\pm 2} = C[I_x \pm iI_y]^2, \end{cases}$$

where

$$C = \frac{eQ}{I(2I-1)}, \quad eQ = \langle II | Q_0 | II \rangle.$$

The only non-vanishing matrix elements of Q_{μ} are $\langle m+\mu | Q_{\mu} | m \rangle$. Here $m\hbar$ and $(m+\mu)\hbar$ represent the eigenvalues of I_z if the direction of the external applied magnetic field is along the z -axis. The coefficients of W_{μ} are functions of the displacement of the nuclei relative to the central nucleus and hence W_{μ} can be developed in powers of r_i .

$$(7) \quad W_{\mu} = A_{\mu} + \sum_i A_{\mu i} \cdot \mathbf{r}_i + \sum_{ij} A_{\mu ij} : \mathbf{r}_i \mathbf{r}_j + \dots$$

The double dot indicates the complete inner product.

Substituting (7) into equation (5), \mathcal{H}' is expressed in powers of the r_i

$$(8) \quad \mathcal{H}' = \mathcal{H}'_0 + \mathcal{H}'_1 + \mathcal{H}'_2 + \dots,$$

where $\mathcal{H}'_0 = \sum_{\mu} A_{\mu} Q_{\mu}$.

The constant term \mathcal{H}'_0 gives rise to the static quadrupolar interaction. This perturbs the originally equally spaced Zeeman levels of the nucleus in the presence of the external magnetic field and leads to splitting of the magnetic resonance line. In the absence of external field only pure quadrupole spectrum occurs. However, relaxation is caused by the higher order terms $\mathcal{H}'_1, \mathcal{H}'_2, \dots$. The linear term \mathcal{H}'_1 in the first order leads to the so-called direct processes in which the nuclear spin makes an upward (downward) transition and one of the lattice oscillators is de-excited (excited). In second order the linear term \mathcal{H}'_1 gives rise to Raman processes where the nuclear transition is accompanied by the simultaneous excitation of one lattice oscillator and de-excitation of another one. The first order effect of \mathcal{H}'_2 gives rise to Raman processes. The contribution due to first and higher order effects of \mathcal{H}'_1 , higher order effects of \mathcal{H}'_2 , and first order effects of $\mathcal{H}'_3, \mathcal{H}'_4, \dots$ are all negligible compared to the first order effect of the quadratic term in \mathcal{H}'_2 , which according to KRANENDOK, is the relevant relaxation process. Processes in which more than two phonons are involved are important only at very high temperatures.

The transition probability $P(m, m+\mu)$ that the nuclear spin makes a transition from the state m to the state $(m+\mu)$ as a result of the Raman processes is given by

$$(9) \quad P(m, m+\mu) = \frac{|Q_{\mu m}|^2}{2\pi^3 d^2 v^2} \int_0^{\omega_m} \frac{k^4 |f(\omega)|^2}{\omega^2} \frac{e^x}{(e^x - 1)^2} M_{\mu}(ka) d\omega,$$

where $Q_{\mu m} = \langle m+\mu | Q_{\mu} | m \rangle$, d = mass density of the crystal, v = velocity of propagation of long wavelength sound waves independent of direction of polarization, $k = 1/\omega$ the wave number of lattice waves. $\varrho(\omega)$ is defined such that the number of lattice oscillators with frequency between ω and $\omega+d\omega$ is given by

$$(10) \quad \varrho(\omega) d\omega = \frac{V}{2\pi^2 v} f(\omega) k^2 d\omega,$$

where V represent the volume of the crystal.

Here $x = \hbar\omega/\mathcal{R}T$,

$$(11) \quad M_{\mu}(ka) = \sum_{ss'} \sum_{ijlm} N_{\mu i j l m} L_{s i l; s' j m}(ka),$$

with

$$(12) \quad L_{sil; s'jm}(ka) = \{B_i(\mathbf{k}, s)B_i(\mathbf{k}, s)\}\{B_j(\mathbf{k}', s')B_m(\mathbf{k}', s')\}, \quad N_{\mu ijl m} = A_{\mu ej} : A_{\mu lm}.$$

Here the $B_i(\mathbf{k}, s)$ are defined by

$$(13) \quad B_i = B_i(\mathbf{k}, s) = \delta(s, 1)(\cos \mathbf{k}_i a_i - 1) + \delta(s, 2) \sin \mathbf{k}_i a_i,$$

where s is a number which is equal to 1 or 2 and $a_i = \mathbf{R}_i - \mathbf{R}_0$, \mathbf{R}_i and \mathbf{R}_0 representing the equilibrium positions of the i th and central nuclei, respectively; \mathbf{k} and \mathbf{k}' represent the directions of wave propagation. The curly brackets in the equation (12) represent averaging over all directions of \mathbf{k} and \mathbf{k}' .

DAS, ROY and GHOSH ROY⁽²⁷⁾ extended Kranendonk's method to body centered cubic structure.

YOSIDA and MORIYA have calculated nuclear relaxation times in ionic crystals on the basis of covalent effects alone. In the covalent state one p -electron is transferred from the closed shell of the halogen ion to one of the neighbouring metal ions and the hole created by the missing electron causes an asymmetric electron distribution which results in a very large field gradient at the site of the halogen nucleus. They introduced a parameter λ which is a measure of the degree of covalency. KANDA⁽²⁸⁾, as matter of fact, has calculated the degree of covalency in each halide from his measurements of chemical shift of halogen ions in several metal halides and shown that the reciprocal of the relaxation time is proportional to the degree of covalency.

Taking as the zeroth approximation the purely ionic state YOSIDA and MORIYA have calculated relaxation times on the basis of perturbation treatment. According to them the third order perturbation is given by

$$(14) \quad \Delta E_3 = \sum_{n, n'} \frac{(g | \mathcal{H}_t | n)(n | \mathcal{H}_q | n')(n' | \mathcal{H}_t | g)}{(E_n - E_g)(E_{n'} - E_g)},$$

where g means the ground state and n, n' are the excited covalent states in which one p -electron on the halogen ion is transferred to the neighbouring n or n' -th metal ion. Here \mathcal{H}_t is the Hamiltonian which causes an electron of the halogen to jump to a neighbouring metal ion. Here terms such as $(n | \mathcal{H}_q | n')$ are usually very small unless $n = n'$. Neglecting such terms

$$(15) \quad \Delta E_3 = \sum_n \frac{\{(g | \mathcal{H}_t | n\}^2}{(E_n - E_g)^2} (n | \mathcal{H}_q | n) = \sum_n \lambda_n (n | \mathcal{H}_q | n) = \sum_\mu Q_\mu \sum_n \lambda_n (n | W_\mu | n),$$

⁽²⁷⁾ T. P. DAS, D. K. ROY and S. K. GHOSH ROY: *Phys. Rev.*, **104**, 1568 (1956).

⁽²⁸⁾ T. KANDA: *Journ. Phys. Soc. Japan*, **10**, 85 (1955).

where $\lambda = |(g|\mathcal{H}_t|n)|^2/(E_n - E_g)^2$ is a measure of the degree of covalency and is regarded as a function of the distance only between the halogen nucleus and the n -th metal nucleus.

The second summation in equation (15), abbreviated as W_μ , is expressed as follows

$$(16) \quad \begin{cases} W_0 = A' \sum_n \lambda_n (n_n^2 - \frac{1}{3}), \\ W_{\pm 1} = 2A' \sum_n \lambda_n n_n (l_n \mp i m_n), \\ W_{\pm 2} = \frac{1}{2} A' \sum_n \lambda_n (l_n \mp i m_n)^2, \end{cases}$$

where l_n , m_n and n_n represent the direction cosines of $\mathbf{R}_n(X_n, Y_n, Z_n)$, which denotes the co-ordinates of n -th metal nucleus and $A' = \frac{3}{10} eC\langle 1/r^3 \rangle_H$.

Expanding these expressions in powers of small deviations from equilibrium positions and retaining second order terms only

$$(17) \quad \begin{cases} W_{\pm 1} = \frac{2A'}{a^2} \sum_n [u \{n^\mp \gamma_n (\delta \mathbf{R}_n)^2 + 2(\mathbf{n} \cdot \delta \mathbf{R}_n) (\gamma_n \delta \mathbf{R}_n^\mp + n^\mp \delta Z_n)\} + \\ \quad \quad \quad + v n^\mp \gamma_n (\mathbf{n} \cdot \delta \mathbf{R}_n)^2 + \lambda \delta Z_n \delta \mathbf{R}_n^\mp], \\ W_{\pm 2} = \frac{A'}{2a^2} \sum_n [u \{(n^\mp)^2 (\delta \mathbf{R}_n)^2 + 4n^\mp \delta \mathbf{R}_n^\mp (\mathbf{n} \cdot \delta \mathbf{R}_n)\} + \\ \quad \quad \quad + v (n^\mp)^2 (\mathbf{n} \cdot \delta \mathbf{R}_n)^2 + \lambda (n^\mp)^2 (\delta \mathbf{R}_n^\mp)^2], \end{cases}$$

where $u = \frac{1}{2} a \lambda' - \lambda$, $v = 4\lambda - \frac{5}{2} a \lambda' + \frac{1}{2} a^2 \lambda''$.

α_n , β_n and γ_n are the direction cosines of the equilibrium position of the n -th metal ion measured from the halogen nucleus, $\delta \mathbf{R}_n(\delta X_n, \delta Y_n, \delta Z_n)$ the displacement vector, $a = |\mathbf{R}_{n0}|$, \mathbf{n} is the unit vector whose components are α_n , β_n and γ_n , $\delta \mathbf{R}_n^\pm = \delta X_n \pm i \delta Y_n$ and $\alpha_n \pm i \beta_n = n^\pm$.

Following Kranendonk's notation, the transition probability is given by

$$(18) \quad P(m, m + \mu) = \frac{A'^2 |Q_{\mu m}|^2}{2\pi^3 a^4 d^2 v^2} \int_0^{\omega_m} \frac{k^4}{\omega^2} \frac{e^x}{(e^x - 1)^2} M_\mu(ka) d\omega,$$

where

$$(19) \quad M_\mu(ka) = \sum_{n, n'} \sum_s \{B_{n\sigma} B_{n\sigma'} B_{n'\sigma} B_{n'\sigma'}\} \sum_{pp'} \omega_{\mu n}^*(\sigma\sigma') \omega_{\mu n'}(\sigma\sigma'),$$

where σ stands for a set of \mathbf{k} (wave factor), p (one of the three directions of polarization) and s , s taking values 1 and 2,

$$B_n(\sigma) = \delta(s, 1)(\cos a \mathbf{k} \cdot \mathbf{n} - 1) + \delta(s, 2) \sin a \mathbf{k} \cdot \mathbf{n}$$

and

$$(20) \quad \left\{ \begin{aligned} \sum_{\nu\nu'} \omega_{1\nu}^*(\sigma\sigma') \omega_{1\nu'}(\sigma\sigma') &= 4[u^2\{15(\alpha_n\alpha_{n'} + \beta_n\beta_{n'})\gamma_n\gamma_{n'} + 2(\alpha_n\alpha_{n'} + \beta_n\beta_{n'})(\mathbf{n}\cdot\mathbf{n}') + \\ &+ 4(\alpha_n^2 + \beta_n^2)\gamma_{n'}^2 + 4\gamma_n\gamma_{n'}(\mathbf{n}\cdot\mathbf{n}')\} + v^2\{\alpha_n\alpha_{n'} + \beta_n\beta_{n'}\}\gamma_n\gamma_{n'}(\mathbf{n}\cdot\mathbf{n}')^2\} + \\ &+ \lambda^2 + uv\{2(\alpha_n\alpha_{n'} + \beta_n\beta_{n'})\gamma_n\gamma_{n'} + 4(\alpha_n\alpha_{n'} + \beta_n\beta_{n'})\gamma_n^2(\mathbf{n}\cdot\mathbf{n}') + \\ &+ 4(\alpha_n^2 + \beta_n^2)\gamma_n\gamma_{n'}(\mathbf{n}\cdot\mathbf{n}')\} + \lambda u\{2(\alpha_n^2 + \beta_n^2) + 4\gamma_n^2\} + 2\lambda v(\alpha_n^2 + \beta_n^2)\gamma_n^2], \\ \sum_{\nu\nu'} \omega_{2\nu}^*(\sigma\sigma') \omega_{2\nu'}(\sigma\sigma') &= u^2[\frac{11}{4}\{-(\alpha_n^2 + \beta_n^2)(\alpha_{n'}^2 + \beta_{n'}^2) + 2(\alpha_n\alpha_{n'} + \beta_n\beta_{n'})^2\} + \\ &+ 4(\alpha_n\alpha_{n'} + \beta_n\beta_{n'})(\mathbf{n}\cdot\mathbf{n}') + 2(\alpha_n^2 + \beta_n^2)(\alpha_{n'}^2 + \beta_{n'}^2)] + \frac{1}{4}v^2\{-(\alpha_n^2 + \beta_n^2)(\alpha_{n'}^2 + \beta_{n'}^2) + \\ &+ 2(\alpha_n\alpha_{n'} + \beta_n\beta_{n'})^2\}(\mathbf{n}\cdot\mathbf{n}')^2 + \lambda^2 + uv\{\frac{1}{2}(\alpha_n - i\beta_n)^2(\alpha_{n'} + i\beta_{n'})^2 + \\ &+ 2(\alpha_n\alpha_{n'} + \beta_n\beta_{n'})(\alpha_n^2 + \beta_n^2)(\mathbf{n}\cdot\mathbf{n}')\} + 4\lambda u(\alpha_n^2 + \beta_n^2) + \frac{1}{2}\lambda v(\alpha_n^2 + \beta_n^2)^2, \end{aligned} \right.$$

which can be simplified further as $(\mathbf{n}\cdot\mathbf{n}') = 0$ for $n \neq \pm n'$ and $(\mathbf{n}\cdot\mathbf{n}') = \pm 1$ for $n = \pm n'$ crystals of the NaCl type. The transition probability, however, is given in the following convenient form

$$(21) \quad P(m, m+\mu) = C_{\mu m} T^{*2} \sum_{n=1}^4 N_{\mu n} D_n(T^*),$$

where

$$\begin{aligned} C_{\mu m} &= 3|Q_{\mu m}|^2/\pi d^2 v^3 a^3 \quad (\text{Kranendonk}), \\ &= A'^2 C^3 |Q_{\mu m}|^2/2\pi^3 a^7 d^2 v^3 \quad (\text{Yosida and Moriya}) \end{aligned}$$

$$T^* = T/\theta, \quad \theta \text{ Debye temperature},$$

$$D_n(T^*) = T^* \int_0^{1/T^*} \frac{x^2 e^x}{(e^x - 1)^2} L_n(eT^*x) dx,$$

$$c = k_m a = (6\pi^2)^{\frac{1}{3}}, \quad \hbar\omega_m = \hbar v k_m = k\theta, \quad c = (q\sqrt{3}\pi^2/2)^{\frac{1}{3}} \\ \text{for NaCl-type} \qquad \qquad \qquad \text{for CsCl-type}$$

$D_n(T^*)$ has been expanded in descending powers of T^* by Kranendonk and is given as follows (for NaCl or simple cubic crystals)

$$(22) \quad \left\{ \begin{aligned} D_1(T^*) &= 0.20 - 0.0071/T^{*2} + \dots \\ D_2(T^*) &= 0.92 - 0.055/T^{*2} + \dots \\ D_3(T^*) &= 0.50 - 0.031/T^{*2} + \dots \\ D_4(T^*) &= 0.28 - 0.017/T^{*2} + \dots \end{aligned} \right.$$

The coefficients $N_{\mu n}$ are given by

$$\begin{aligned}
 N_{\mu 1} &= \sum (\pm) N_{\mu i l m} ; & N_{\mu n} &= \sum N_{\mu i j l m} ; & (n = 2, 3, 4), \\
 N_{\mu i j l m} &= A_{\mu i j} \cdot A_{\mu l m} , \\
 A_{\mu i j} &= 0 \text{ for } i \neq j, & A_{-\mu i i} &= A_{\mu i i}^* , & A_{\mu -i -i} &= A_{\mu i i} , \\
 A_{0 i i} &= A \begin{vmatrix} a_i & 0 & 0 \\ 0 & b_i & 0 \\ 0 & 0 & c_i \end{vmatrix} ; & A_{1 i i} &= A \begin{vmatrix} 0 & 0 & c'_i \\ 0 & 0 & f'_i \\ e'_i & f'_i & 0 \end{vmatrix} ; & A_{2 i i} &= A \begin{vmatrix} a''_i & d''_i & 0 \\ d''_i & b''_i & 0 \\ 0 & 0 & c''_i \end{vmatrix} ; \\
 A &= q/16a^5 ,
 \end{aligned}$$

where a is the equilibrium distance between the nearest neighbours. According to YOSIDA and MORIYA, the coefficients $N_{\mu n}$ are given by

$$(23) \quad \begin{cases} N_{\mu 1} = N_{\mu 2} = \sum_{\substack{n, n' \\ n = \pm n'}} \sum_{pp'} \omega_{\mu n}^*(\sigma\sigma') \omega_{\mu n'}(\sigma\sigma') , \\ N_{\mu 3} = N_{\mu 4} = \sum_{\substack{n, n' \\ n \neq \pm n'}} \sum_{pp'} \omega_{\mu n}^*(\sigma\sigma') \omega_{\mu n'}(\sigma\sigma') , \end{cases}$$

which after somewhat lengthy calculations are expressed as functions of λ , λ' and λ''

$$(24) \quad \left\{ \begin{aligned} N_{11} &= N_{12} = 48\lambda^2 \left[\left\{ 1 - \frac{4}{3} \left(\frac{a\lambda'}{\lambda} \right) + \frac{2}{3} \left(\frac{a\lambda'}{\lambda} \right)^2 \right\} + \right. \\ &\quad \left. + 2\alpha \left\{ 1 + \frac{1}{3} \left(\frac{a\lambda'}{\lambda} \right) - \frac{1}{2} \left(\frac{a\lambda'}{\lambda} \right)^2 + \frac{1}{12} \left(\frac{a^2\lambda''}{\lambda} \right)^2 \right\} \right] , \\ N_{14} &= 32\lambda^2 \left[\left\{ -1 + \left(\frac{a\lambda'}{\lambda} \right)^2 \right\} + \right. \\ &\quad \left. + 5\alpha \left\{ 1 - \frac{9}{20} \left(\frac{a\lambda'}{\lambda} \right)^2 + \frac{3}{5} \left(\frac{a^2\lambda''}{\lambda} \right) - \frac{1}{10} \left(\frac{a^2\lambda''}{\lambda} \right) \left(\frac{a\lambda'}{\lambda} \right) \right\} \right] , \\ N_{21} &= N_{22} = 18\lambda^2 \left[\left\{ 1 - \frac{7}{9} \left(\frac{a\lambda'}{\lambda} \right) + \frac{5}{18} \left(\frac{a\lambda'}{\lambda} \right)^2 + \frac{1}{30} \left(\frac{a^2\lambda''}{\lambda} \right)^2 \right\} - \right. \\ &\quad \left. - \frac{1}{3} \alpha \left\{ 1 + \frac{1}{3} \left(\frac{a\lambda'}{\lambda} \right) - \frac{1}{2} \left(\frac{a\lambda'}{\lambda} \right)^2 + \frac{1}{12} \left(\frac{a^2\lambda''}{\lambda} \right)^2 \right\} \right] , \\ N_{24} &= 2\lambda^2 \left[\left\{ 1 + \frac{7}{4} \left(\frac{a\lambda'}{\lambda} \right)^2 + 3 \left(\frac{a^2\lambda''}{\lambda} \right) - \frac{1}{2} \left(\frac{a^2\lambda''}{\lambda} \right) \left(\frac{a\lambda'}{\lambda} \right) \right\} - \right. \\ &\quad \left. - 5\alpha \left\{ 1 - \frac{9}{20} \left(\frac{a\lambda'}{\lambda} \right)^2 + \frac{3}{5} \left(\frac{a^2\lambda''}{\lambda} \right) - \frac{1}{10} \left(\frac{a^2\lambda''}{\lambda} \right) \left(\frac{a\lambda'}{\lambda} \right) \right\} \right] . \end{aligned} \right.$$

The degree of covalency λ is a function of the distance between the ions and is estimated from the chemical shift of the halogen nucleus. Assuming $\lambda \propto \exp[-R/0.345]$, where R is the interionic distance in Å units, such that $\lambda'/\lambda = -1/0.345$ and $\lambda''/\lambda = (1/0.345)^2$, YOSIDA and MORIYA have calculated the coefficient $N_{\mu n}$.

The relaxation time τ can be defined by $\tau = 1/\bar{P}$, where \bar{P} is the average value of P , averaged over all values of m and μ as the relaxation time in the presence of quadrupolar interaction is not unique. However, Kranendonk's values of relaxation times in the absence of covalent and polarization effects ($\gamma = 1$) are about 4 to 6 orders of magnitude larger than those observed. In order to account for the experimental relaxation times, he assumes multiplication factor γ of the order of $10^2 \div 10^3$. The values of nuclear relaxation times in ionic crystals calculated by YOSIDA and MORIYA on the basis of covalent bonding effects alone are about 3 to 10 times larger than the observed ones. This discrepancy is traced in the simple Debye treatment of the lattice vibrations and ambiguities in the determinations of the Debye temperature θ or sound velocity v . The interaction of the covalent electron with the quadrupole moment is assumed to be unaffected by shielding and anti-shielding effects and the relaxation time is attributed to covalent effects alone.

KRAUS and TANTTILA⁽²⁸⁾ have computed the probability per unit time that the sound waves will produce a transition of a nuclear spin between its Zeeman levels. The nuclear quadrupolar interaction Hamiltonian is given by

$$(25) \quad \mathcal{H} = \sum_{\alpha} \frac{q_{\alpha}}{(r^{(\alpha)})^5} \sum_{i=-2}^2 C_i Q_i B_{-i}^{(\alpha)},$$

where q_{α} is an external charge to a nucleus N , $r^{(\alpha)}$ is the distance between the nuclear center of mass and the external charge q_{α} when both of them are displaced by sound waves, C_i are numerical constants, Q_i are the components of the nuclear quadrupole moment given by $Q_i \equiv \int \varrho_n(r) A_i d\tau_n$, ($i = 0, \pm 1, \pm 2$). The quadrupolar term of the electrostatic potential at a position r_n from the center of mass of the nucleus, where ϱ_n is the nuclear charge density due to the charge q_{α} after displacement, is given by

$$(26) \quad V_{\alpha} = \frac{q_{\alpha}}{6(r^{(\alpha)})^5} \mathbf{A} : \mathbf{B},$$

where \mathbf{A} and \mathbf{B} are second rank symmetric tensors.

(28) O. KRAUS and W. H. TANTTILA: *Phys. Rev.*, **109**, 1052 (1958).

The matrix elements of the operator \mathcal{H} which are of interest are given by

$$(27) \quad \begin{cases} (I_m | \mathcal{H} | I_{m+2}) = (I_m | Q_{-2} | I_{m+2}) \sum_{\alpha} \frac{q_{\alpha}}{R_{\alpha}^5} C_2 B_{+2}^{(\alpha)}, \\ (I_m | \mathcal{H} | I_{m-2}) = (I_m | Q_{+2} | I_{m-2}) \sum_{\alpha} \frac{q_{\alpha}}{R_{\alpha}^5} C_2 B_{-2}^{(\alpha)}. \end{cases}$$

The displacement of a lattice point in the presence of unidirectional standing sound waves being propagated along the x -axis is given by

$$S = A \cos(kx - \delta) \cos \omega t,$$

where $k = 2\pi/\lambda$ with λ the wavelength of the sound waves, A the amplitude of the sound waves and δ an arbitrary phase factor. The displacement of the nucleus is taken as $S_1^{(0)} = A \cos \delta \cos \omega t$ and for the charge q , as $S_1^{(1)} = A \cos(ka - \delta) \cos \omega t$.

Expanding $B_{+2}^{\alpha}/R_{\alpha}^5$ and $B_{-2}^{\alpha}/R_{\alpha}^5$ in terms of the relative displacement of q_{α} and utilizing the fact that

$$(28) \quad \begin{cases} (I_m | Q_{+2} | I_{m-2}) = \frac{3eQ}{I(2I-1)} [(I-m+2)(I+m-1)(I-m+1)(I+m)]^{\frac{1}{2}}, \\ (I_m | Q_{-2} | I_{m+2}) = \frac{3eQ}{I(2I-1)} [(I+m+2)(I-m-1)(I+m+1)(I-m)]^{\frac{1}{2}}, \end{cases}$$

the matrix elements are given by

$$(29) \quad \begin{cases} (I_m | \mathcal{H} | I_{m+2}) = \frac{-e^2 Q \gamma}{8I(2I-1)} \cdot [(I+m+2)(I-m-1)(I+m+1)(I-m)]^{\frac{1}{2}} \frac{18}{a^3} A k \sin \delta \cos \omega t, \\ (I_m | \mathcal{H} | I_{m-2}) = \frac{-e^2 Q \gamma}{8I(2I-1)} \cdot [(I-m+2)(I+m-1)(I-m+1)(I+m)]^{\frac{1}{2}} \frac{18}{a^3} A k \sin \delta \cos \omega t. \end{cases}$$

where $q_{\alpha} = \gamma e$.

From the first order perturbation theory the probability that in time t the nucleus will make a transition from the initial state m to one of the states k is given by

$$(30) \quad P_{km} = \frac{|\mathcal{H}^0|^2}{\hbar^2} g(\omega) \frac{\pi}{2} t,$$

where \mathcal{H}^0 is time independent and $g(\omega)$ is the normalized shape function of the nuclear resonance line. Averaging over the frequency spread $\delta\omega$ of the resonance line the average transition probability per unit time \bar{P} is given by

$$(31) \quad \bar{P} = |\mathcal{H}_{km}^0|^2 / 4\hbar^2 \delta\nu.$$

Thus the transition probability per unit time for $\Delta m = \pm 2$ transitions is given by

$$(32) \quad \left\{ \begin{array}{l} P(m, m-2) = \frac{81}{64\hbar^2 \delta\nu} \frac{e^4 Q^2 \gamma^2}{I^2 (2I-1)^2} \cdot \\ \quad \cdot (I-m+2)(I+m-1)(I-m+1)(I+m) \frac{A^2 k^2}{a^6} \sin^2 \delta, \\ P(m, m+2) = \frac{81}{64\hbar^2 \delta\nu} \frac{e^4 Q^2 \gamma^2}{I^2 (2I-1)^2} \cdot \\ \quad \cdot (I+m+2)(I-m-1)(I+m+1)(I-m) \frac{A^2 k^2}{a^6} \sin^2 \delta. \end{array} \right.$$

KRAUS and TANTTILA have also derived expressions for the equilibrium nuclear magnetisation in the presence of ultrasonic and thermal lattice vibrations. The time rate-of-change of the z -component, m_z , of the macroscopic magnetisation, which arises from the nuclear spin system is given by

$$(33) \quad \frac{dm_z}{dt} = \frac{dm_z}{dt} \Big|_{\Delta m = \pm 1} + \frac{dm_z}{dt} \Big|_{\Delta m = \pm 2} + \frac{dm_z}{dt} \Big|_{\text{ultrasonic}},$$

where

$$\begin{aligned} \frac{dm_z}{dt} \Big|_{\Delta m = \pm 1} &= \frac{6(m_{z_0} - m_z)}{I(I+1)(2I+1)} \sum_{m=l}^{-l+1} \omega_{m-1}^m, \\ m_{z_0} &= \frac{1}{3} \gamma \hbar I(I+1) n(\hbar\omega/KT_l), \end{aligned}$$

= value of m_z when the spin system is in thermal equilibrium with the lattice,

T_l = Temperature of the lattice.

Here ω_{m-1}^m is the probability per unit time for a thermally induced transition of a spin from the state m to the state $m-1$ and given by

$$(34) \quad \omega_{m-1}^m = \frac{9e^2 Q^2}{4I^2 (2I-1)^2} (2m-1)^2 (I+m)(I-m+1) F(l),$$

where $F(l)$ is a function of the lattice co-ordinates only.

Similarly $(dm_z/dt)|_{\angle m=\pm 2}$ is given by

$$(35) \quad \left. \frac{dm_z}{dt} \right|_{\angle m=\pm 2} = \frac{24(m_{z_0} - m_z)}{I(I+1)(2I+1)} \sum_{m=-I}^{-I+2} \omega_{m-2}^m,$$

where

$$\omega_{m-2}^m = \frac{9e^2 Q^2}{I^2(2I-1)^2} (I+m)(I-m+1)(I+m-1)(I-m+2)G(l),$$

and again $G(l)$ is a function of the co-ordinates only.

If the frequency of the sound waves is chosen in such a way that it produces $\Delta m = \pm 2$ transitions

$$(36) \quad \left. \frac{dm_z}{dt} \right|_{\text{ultrasonic}} = \frac{-24}{I(I+1)(2I+1)} m_z \sum_{m=-I}^{-I+2} P_{m-2}^m,$$

where the ultrasonic probabilities are given by equations (32).

Introducing relaxation times dm_z/dt can be expressed as

$$(37) \quad \frac{dm_z}{dt} = \frac{m_{z_0} - m_z}{T_1} - \frac{m_z}{T_u},$$

where

$$(38) \quad \begin{cases} \frac{1}{T_1} = \frac{1}{T'} + \frac{1}{T''}, \\ \frac{1}{T'} = \frac{6}{I(I+1)(2I+1)} \sum_{m=-I}^{-I} \omega_{m-1}^m, \\ \frac{1}{T''} = \frac{24}{I(I+1)(2I+1)} \sum_{m=-I}^{-I+2} \omega_{m-2}^m, \\ \frac{1}{T_u} = \frac{24}{I(I+1)(2I+1)} \sum_{m=-I}^{-I+2} P_{m-2}^m. \end{cases}$$

Here T_1 is the observed spin-lattice relaxation time. Ultrasonic relaxation time can be computed from equations (38) and (32).

If the ultrasonic excitation which is applied to the specimen is constant and the time through which it is applied is longer than T_1 , the magnetization is constant in a region where $\delta = \text{constant}$. Thus putting $dm_z/dt = 0$, we obtain

$$(39) \quad m_z = \frac{m_{z_0}}{1 + (T_1/T_u)} = \frac{m_{z_0}}{1 + \beta \sin^2 \delta},$$

where

$$(40) \quad \beta = \frac{T_1}{\sin^2 \delta} \frac{24}{I(I+1)(2I+1)} \sum_{m=I}^{-I+2} P_{m-2}^m.$$

The total magnetisation is obtained by integrating equation (39) over the volume of the crystal and is given by

$$(41) \quad M_z = \int m_z dT = m_{z_0} \int \frac{A dx}{1 + \beta \sin^2 [(2\pi/\lambda)x]} = \frac{M_{z_0}}{(1 + \beta)^{\frac{1}{2}}},$$

where A is the cross-sectional area of the uniform cylinder, $\delta = 2\pi x/\lambda$, λ = ultrasonic wavelength, M_{z_0} = total magnetisation of nuclei in the absence of ultrasonic excitation.

ABRAGAM and PROCTOR⁽³⁰⁾ have also deduced the ratio (M_z/M_{z_0}) without going into the exact expressions for the contributions to the rates of change of populations from the spin-lattice relaxation and spin-spin coupling. The rates of change of population of the levels $I_z = m$ of ^{23}Na irradiated by ultrasonic waves at twice the Larmor frequency are given by

$$(42) \quad \begin{cases} \frac{dn_{\frac{3}{2}}}{dt} = -W(n_{\frac{3}{2}} - n_{-\frac{3}{2}}) + F_{\frac{3}{2}}(n_m) + G_{\frac{3}{2}}(n_m), \\ \frac{dn_{\frac{1}{2}}}{dt} = -W(n_{\frac{1}{2}} - n_{-\frac{1}{2}}) + F_{\frac{1}{2}}(n_m) + G_{\frac{1}{2}}(n_m), \\ \frac{dn_{-\frac{1}{2}}}{dt} = -W(n_{-\frac{1}{2}} - n_{-\frac{3}{2}}) + F_{-\frac{1}{2}}(n_m) + G_{-\frac{1}{2}}(n_m), \\ \frac{dn_{-\frac{3}{2}}}{dt} = -W(n_{-\frac{3}{2}} - n_{\frac{1}{2}}) + F_{-\frac{3}{2}}(n_m) + G_{-\frac{3}{2}}(n_m), \end{cases}$$

where F_m and G_m represent the contributions to the rates of change of the populations from the spin-lattice relaxation and spin-spin coupling, respectively. Writing $\langle M_z \rangle = \frac{3}{2}(n_{\frac{3}{2}} - n_{-\frac{3}{2}}) + \frac{1}{2}(n_{\frac{1}{2}} - n_{-\frac{1}{2}})$, the contribution of spin-lattice relaxation to the rate of change of $\langle M_z \rangle$, i.e.,

$$\frac{3}{2}F_{\frac{3}{2}}() + \dots + \left(-\frac{3}{2}\right)F_{-\frac{3}{2}} = -\frac{\langle M_z \rangle - M_{z_0}}{T_1},$$

provided a single spin-lattice relaxation is assumed, we obtain

$$(43) \quad \frac{d\langle M_z \rangle}{dt} = -\frac{\langle M_z \rangle - M_{z_0}}{T_1} - 2W\{(n_{\frac{3}{2}} - n_{-\frac{3}{2}}) + (n_{\frac{1}{2}} - n_{-\frac{1}{2}})\},$$

(30) A. ABRAGAM and V. G. PROCTOR: *Phys. Rev.*, **109**, 1441 (1958).

as the contributions due to spin-spin interaction is zero because of conservation of energy. As Boltzmann distribution is maintained throughout

$$(n_{\frac{3}{2}} - n_{-\frac{3}{2}}) = 3(n_{\frac{1}{2}} - n_{-\frac{1}{2}}) \quad \text{and consequently} \quad \langle M_z \rangle = \frac{10}{6} (n_{\frac{3}{2}} - n_{-\frac{3}{2}})$$

or

$$(44) \quad \frac{d}{dt} \langle M_z \rangle = - \frac{\langle M_z \rangle - M_{z_0}}{T_1} - \frac{8W}{5} \langle M_z \rangle.$$

The limiting value of $\langle M_z \rangle$ is given by putting $d\langle M_z \rangle/dt = 0$

$$\langle M_z \rangle / M_{z_0} = (1 + 8WT_1/5)^{-1}.$$

Since the signal amplitude ξ is proportional to $\langle M_z \rangle$, we have

$$(45) \quad \xi/\xi_0 = \langle M_z \rangle / M_{z_0} = \left(1 + \frac{8WT_1}{5}\right)^{-1}.$$

3. - Experimental technique.

The technique is essentially based upon the pulsed nuclear induction method of measuring nuclear magnetization as described by HAHN⁽³¹⁾. The thing to be remembered is that if a short pulse of radio frequency magnetic field is applied at the Larmor frequency, the transient nuclear induction signal is proportional in magnitude to the static magnetization of the system, which is a function of the population of the various states. Thus the amplitude of the transient nuclear induction signal A_1 following the pulse of radio frequency flux is proportional to the population difference between the quadrupole states at thermal equilibrium. Once the equilibrium is disturbed the instantaneous population difference Δ will try to reach its equilibrium value Δ_e at a rate which is determined by the thermal relaxation time T_1 according to the relation

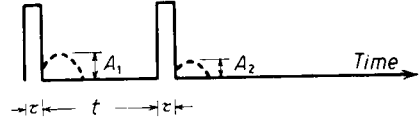
$$(46) \quad \frac{\Delta(t)}{\Delta_e} = (1 - \exp[-t/T_1]),$$

provided the time interval between the two successive radio frequency pulses is greater than the thermal relaxation time T_1 and $\Delta(0) = 0$ which is the case when the pulse length τ is adjusted to give maximum transient in-

(31) E. L. HAHN: *Phys. Rev.*, **77**, 297 (1949).

duction signal. If A_2 is the amplitude of the transient nuclear induction signal after a second pulse of radio frequency flux of the same duration is applied after a time t (see Fig. 1), then

$$(47) \quad \frac{A_2}{A_1} = (1 - \exp[-t/T_1]).$$



By measuring the ratio (A_2/A_1) as a function of the time interval t and plotting $\log_e (1 - A_2/A_1)$ vs. t , the thermal relaxation T_1 is known from the slope of the straight line.



Fig. 1.

Next the ultrasonic excitation is applied at twice the Larmor frequency and the magnetization is again measured. The typical time sequence of events is shown in Fig. 2. If ξ_0 is the amplitude of the nuclear induction signal in the absence of ultrasonic excitation and ξ , in the presence of ultrasonic excitation, the ratio can be expressed as

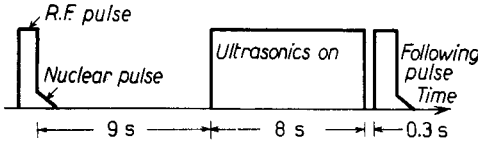


Fig. 2.

$$(48) \quad \left(\frac{\xi_0}{\xi}\right)^2 = 1 + k_1 V^2,$$

where V is the peak voltage applied to the transducer. If we put

$M_z = \xi_0$, $M_z = \xi$ and $dM_z/dt = 0$ in equation (41), we obtain

$$(49) \quad k_1 V^2 = \beta_1 = \frac{243}{8a^6 \hbar^2 \delta\nu} \frac{e^4 Q^2 \gamma^2 A^2 k^2}{I^3 (I+1)(2I+1)(2I-1)^2} T_1 \cdot \\ \cdot (I-m+2)(I+m-1)(I-m+1)(I+m),$$

where $\delta\nu$ is the ultrasonic line width, A is the amplitude of ultrasonic vibrations, $k = 2\pi a/\lambda$, λ is the ultrasonic wavelength, a is the lattice constant, e is the electronic charge and the nearest neighbours of a given nucleus are replaced by point charges of magnitude γe .

Thus from the experimentally measured values of k_1 (which is known from the slope of the curve $(\xi_0/\xi)^2$ vs. V^2), V , $\delta\nu$ (which is known from the plot of (ξ/ξ_0) vs. ultrasonic frequency at constant power around $2\nu_0$, ν_0 being the nuclear magnetic resonance frequency), k and T_1 , one can obtain the information about the parameter γ provided the amplitude of ultrasonic vibrations in the crystal is known. Ultrasonic energy density in the crystal is calculated from the power transmitted to the crystal and the phonon relaxation times of the ultrasonic phonons from the relation

$$(50) \quad V' \mathcal{E} = P_s T_\rho,$$

where V' is the volume of the specimen, \mathcal{E} is the ultrasonic energy density, P_s is the power delivered to the specimen, T_ϕ the sound attenuation coefficient or phonon relaxation time. The power delivered to the sample is known in terms of the voltage across the quartz and is given by

$$(51) \quad P_s = \frac{R_e^{\text{eff}}}{(R_u^{\text{eff}} + R_e^{\text{eff}})^2} V^2,$$

where R_e^{eff} is the effective load resistance and R_u^{eff} is the effective internal resistance of the quartz and its circuits. The sound attenuation coefficients are known from measurements of HUNTINGTON⁽³²⁾ and GALT⁽³³⁾. PROCTOR

and ROBINSON⁽³⁴⁾ have also measured it by studying the attenuation of the nuclear induction signal as a function of the frequency of ultrasonic excitation both when one face of the specimen is or is not in contact with castor oil. In the former case since some of the acoustic energy escapes into oil, the attenuation of the nuclear induction signal is less. From a knowledge of acoustic impedances of NaCl and castor oil and from the loss of attenuation of the nuclear induction signal they calculated the value of 10 MHz phonon relaxation time which is in good agreement with the values obtained by HUNTINGTON and GALT.

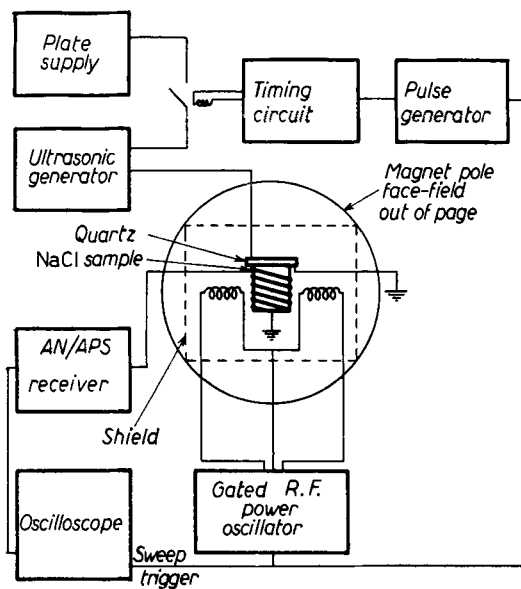


Fig. 3.

The block diagram of the apparatus which has been used by PROCTOR and his associates is given in Fig. 3. It consists of two main groups, one which is used in producing ultrasonic excitation and the other which measures the nuclear magnetization. A nuclear induction head of the type described by WEAVER⁽³⁵⁾ is used. The transmitter and the receiving coils are at right angles to each other and a static magnetic field is applied perpendicular to

(32) H. B. HUNTINGTON: *Phys. Rev.*, **72**, 311 (1947).

(33) J. K. GALT: *Phys. Rev.*, **73**, 1460 (1948).

(34) W. G. PROCTOR and W. A. ROBINSON: *Phys. Rev.*, **104**, 1344 (1956).

(35) H. E. WEAVER: *Phys. Rev.*, **89**, 923 (1953).

the axes of both the coils. The quartz crystal is glued to one end of an NaCl rod of about $\frac{1}{2}$ in. diameter and one in. length which serves the purpose of an extension the of ultrasonic path length for convenience. The other end of this rod is cemented to the sample crystal of the same diameter. The sample crystal is well insulated from the ultrasonic circuits. PROCTOR and ROBINSON used a steady magnetic field of 4220 oersteds and a short pulse of 50 μ s of radio frequency magnetic field at the Larmor frequency 4.75 MHz for studying the transient radio frequency nuclear signal whose magnitude is proportional to the nuclear magnetization just before the pulse. Ultrasonic excitation was applied nine seconds after the preceding nuclear magnetization measurement, at twice the Larmor frequency for 8 seconds and after a delay of 0.03 second the nuclear magnetization was again measured (see Fig. 2).

4. - Results and discussions.

The data on ultrasonic investigation of nuclear spin-lattice relaxation time are very limited. The only crystals in which ultrasonic excitation has been used to study its effects on nuclear spin-lattice relaxation are NaCl, NaI, NaClO₃ and InSb. NaClO₃ was the first crystal to be studied by PROCTOR and TANTTILA. They observed that the population difference of the two pure quadrupole levels decreased when the sample was subjected to ultrasonic energy at the transitions corresponding to $\Delta m = \pm 1$ and $\Delta m = \pm 2$. However, it was realised that the magnetic fields due to currents in the ultrasonic system might affect the population difference. Consequently PROCTOR and ROBINSON used ultrasonic excitation corresponding to $\Delta m = \pm 2$ transitions in the case of NaCl and the specimen too was placed in a static magnetic field.

Assuming that the quadrupolar relaxation is the most important mechanism in NaCl, PROCTOR and ROBINSON calculated γ on the basis of Kranendonk's six point model. The value of γ comes out to be equal to 3 which is somewhat lower than the value of 50 estimated by KRANENDONK. However, as he points out, his value is a measure of the second derivative of the electric field gradient whereas the value of γ which is calculated from ultrasonic measurements is a measure of the first derivative. The discrepancy can also be attributed to the lack of reliable measurements of ultrasonic attenuation as reported in the literature and in the ambiguity in equating phonon relaxation times with ultrasonic attenuation. In view of the fact that the knowledge of the amplitude of ultrasonic vibrations in the crystal helps a great deal in determining the strength of the coupling, it should be known more accurately than what is possible now. However, if one does not care for the absolute value of the quadrupolar coupling the problem of determining the correct

value of ultrasonic energy or amplitude in the crystal can be avoided by comparing the net magnetizations of two sets of nuclei in equilibrium with thermal and lattice vibrations caused by ultrasonic waves in the direction of a constant external magnetic field H_0 . This was done in the case of NaI crystal by JENNINGS, TANTTILA and KRAUS ⁽³⁶⁾. They determined experimentally the equilibrium magnetizations in the direction of the static external magnetic field of sodium and iodine nuclei as a function of the ultrasonic power delivered to the sodium iodide crystal which in turn is proportional to the square of the peak voltage applied to the quartz crystal. By plotting $(\xi_0/\xi)^2$ vs. V for both sodium and iodine nuclei, the slopes k_{Na} and k_I are known. However, the ratio of the two slopes is given by

$$(52) \quad \frac{k_I}{k_{Na}} = \frac{T_{II}}{T_{INa}} \cdot \frac{Q_I^2 \gamma_I^2}{\delta \nu_I} \cdot \frac{\delta \nu_{Na}}{Q_{Na}^2 \gamma_{Na}^2} (0.240),$$

provided we assume that the amplitude of ultrasonic vibrations A is proportional to the applied voltage ($A = CV$, where C is a constant). JENNINGS, TANTTILA and KRAUS obtain the following values experimentally: $T_{II} = 0.0065$ s, $T_{INa} = 5$ s, $(k_I/k_{Na}) = 2.2$, $\delta \nu_{Na} = 4.65$ kHz/s, $\delta \nu_I = 4.49$ kHz/s. Substituting these values together with values for quadrupole moments for sodium and iodine nuclei, they obtain

$$(\gamma_I/\gamma_{Na}) = 10.9,$$

which is in qualitative agreement with the theoretical calculations of STERNHEIMER ⁽³⁷⁾ and DAS and BERSOHN ⁽³⁸⁾. However, k is to be compared with $1 + \gamma_\infty$ where γ_∞ is the polarization calculated by STERNHEIMER. According to Sternheimer's calculations, γ_∞ for sodium ions is 4.2. Though he does not give any calculation for iodide ion, yet it can be guessed from the corresponding value in the cesium ion, in which case he obtains $\gamma_\infty = 143$. Supposing that the γ_∞ for the iodide ions is not less than 143, $(\gamma_I/\gamma_{Na}) = 28$ according to Sternheimer's calculations. The discrepancy between the two results can, however, be traced in the simplified theoretical model which has been used by JENNINGS, TANTTILA and KRAUS. Moreover, imperfections in the crystal which are known very well to cause broadening effects on the satellite lines of iodine nuclei should also be taken into consideration. Imperfections in the crystal give rise to random but permanent electric field gradients which interact with nuclear quadrupole moments. This might contribute in the right direction towards the increase in the ratio of (γ_I/γ_{Na}) . However, in the treat-

⁽³⁶⁾ D. A. JENNINGS, W. H. TANTTILA and O. KRAUS: *Phys. Rev.*, **109**, 1059 (1958).

⁽³⁷⁾ R. M. STERNHEIMER: *Phys. Rev.*, **105**, 158 (1957).

⁽³⁸⁾ T. P. DAS and R. BERSOHN: *Phys. Rev.*, **102**, 733 (1956).

ment given by KRAUS and TANTTILA, the spin system has been assumed to have a uniform temperature, which may not be valid in view of the fact that ultrasonic excitation causes hot spots in the system and the spin conduction cannot be neglected.

The above calculations are based on the concept of a spin temperature as distinct from lattice temperature whose validity has been discussed in great detail by ABRAGAM and PROCTOR⁽³⁹⁾. The existence of spin temperature as a valid assumption leads to certain predictions which can be tested experimentally. For nuclei $I > \frac{1}{2}$ the equidistance of the levels $I_z = m$ of a spin in a magnetic field H_0 makes it possible to define the spin temperature according to the relation

$$P_m \sim \exp \{ - \gamma \hbar H_0 m / kT \},$$

where the populations P_m of these levels form a Boltzmann distribution. The Boltzmann distribution of the levels is maintained and even if it is not so initially at $t = 0$, spin-spin interactions bring it to that form. The test of such an effect is provided by ultrasonic saturation experiments. Equation (45), which is derived on the assumption of Boltzmann distribution shows that M tends to zero as the ultrasonic transition probability becomes sufficiently strong. ABRAGAM and PROCTOR have been able to increase the density of ultrasonic waves in the crystal to such an extent that the magnetic moment of ^{23}Na completely disappears. Ultrasonic experiments illustrate the role of the spin-spin interaction in establishing and maintaining a Boltzmann distribution between the populations of the spin system.

PROCTOR and ROBINSON have also attempted to seek information regarding the number of imperfections in the crystal from ultrasonic line width. ROBINSON⁽³⁹⁾ has shown that the average field gradient caused by dislocations is approximately given by $q \sim 6e\gamma\zeta^{1/2}/a^2$, where ζ is the number of dislocations per square centimeter. Equating the line width to twice the pure quadrupole interaction energy $eqQ/2$, the line width is given by

$$\Delta\nu \sim \frac{6e^2\gamma Q\zeta^{1/2}}{a^2\hbar}.$$

PROCTOR and ROBINSON obtain the ultrasonic line width in NaCl equal to 4 kHz. Using this value ζ comes out to be equal to $\sim 10^{10}$ dislocations/cm², which is in fair agreement with the values obtained by other methods.

MENES and BOLEF⁽⁴⁰⁾ studied the absorption of acoustic energy at the

⁽³⁹⁾ W. A. ROBINSON: *Thesis* (University of Washington, 1956), unpublished.

⁽⁴⁰⁾ M. MENES and D. I. BOLEF: *Phys. Rev.*, **109**, 218 (1958).

resonant frequency of ^{115}In nuclei in a single crystal of InSb at both the normal nuclear magnetic resonance frequency ($\Delta m = \pm 1$) and at the double frequency ($\Delta m = \pm 2$). The nuclear resonance acoustic absorption was studied by the change in the mechanical Q of the sample, which changed the electrical impedance of the transducer which controlled the Q of the tank circuit of a modified Pound-Watkins type of spectrometer.

So far the ultrasonic excitation has been applied in only one fixed direction, say the 100 direction, but if it is applied in different directions (*), the picture which we may get with regard to anisotropy of γ in the crystal may yield interesting information on electron distributions and their relative displacement under ultrasonic excitation. It will be further interesting if ultrasonic excitation is applied to solids where spin-lattice relaxation is due to magnetic dipole interaction. So far as the improvements in the technique are concerned, some better ways are yet to be devised which may give reliable values of amplitudes of ultrasonic waves in the crystal or displacements of lattice points under ultrasonic excitation.

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Part of this work was carried out while the author was at Western Reserve University, Cleveland, Ohio, U.S.A. The author gratefully acknowledges a grant from Office of Naval Research which made his stay in Cleveland possible. The author is also grateful to Professor ERNEST YEAGER for his helpful comments and suggestions.

(*) *Note added in proof.* — Recently TAYLOR and BLOEMBERGEN (*Phys. Rev.*, **113**, 431 (1959)), have studied nuclear spin saturation by Ultrasonics in NaCl crystal. They found no angular dependence in the saturation curves. They have been successful in measuring the components of the fourth order tensor S , which connects the electric field gradient tensor at the nucleus with the strain deformation tensor ϵ

$$\nabla_i \nabla_j V = \sum_{k,l} S_{ijkl} \epsilon_{kl}, \quad (i, j, k, l = x, y, z) -$$

Absence of angular dependence implies that $S_{44}/S_{11} = \frac{3}{2}$, which differs from Cauchy relation $S_{44}/S_{11} = -\frac{1}{2}$. Also the experimental ratio $(S_{11})_{\text{ex}}/(S_{11})_{\text{Na}} = 1.8$, whereas the ionic point-charge model coupled with an isotropic Sternheimer antishielding factor gives a factor 10. The results show inadequacy of ionic point-charge model and indicate the possibility of a considerable amount of covalent character and configurational interaction on the Na^+ ion.