The Multiple Phonon-Spin Excitation Mechanism in GaAs

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Summary: Nuclear spin transitions are induced normally by phonons radiated into the crystal at a quadrupolar transition frequency. Non-linear nuclear spin transitions are induced when, e. g., the difference frequency of intense 25 MHz and 10 MHz phonons is equal to the transition frequency. These experiments are briefly reviewed and the possible mechanisms for the non-linear nuclear spin excitation are discussed. The dominant mechanism is the creation of phonons at the transition frequency by non-Hookes law crystal binding forces. However the Raman process, which is responsible for the quadrupolar spin-lattice relaxation, is also possible. It is shown that the ratio of the transition probability for two different nuclear species in the same crystal is the same, for the normal and non-linear spin excitations, if the mechanism involves the Raman process. If the non-Hookes law forces are important, then the two ratios will be different for the normal and non-linear spin excitations. Experimental results are presented which clearly indicate that the multiple phonon-nuclear spin excitation mechanism is due to the creation of transition frequency phonons by the non-Hookes law crystal forces.

Section I (Introduction)

Nuclear spin transitions have been previously induced by irradiating phonons into a crystal at the Larmor frequency ν_0 or at $2\,\nu_0$ [1][1]). The phonons modulate the electric field gradient, which is coupled to the quadrupole moment of the nucleus. When the electric field gradient varies in time at one of these two quadrupole transition frequencies, nuclear spin transitions are induced. In this way phonons irradiated into the crystal can cause a saturation of the nuclear magnetic resonance signal.

However nuclear spin transitions have also been induced by the simultaneous irradiation of phonons into a crystal at two different, non-resonant frequencies [2–4]. These transitions are observed when the sum or difference frequency of the phonons is equal to one of the two quadrupole transitions frequencies. It is the purpose of this paper to describe an experiment [5] which shows the non-linear mechanism through which these spin transitions do occur. This method compares the excitation sensitivity of Ga^{69} and As^{75} in GaAs when excited by phonons at $2\,\nu_0$ and when excited by phonons at $\nu_1 - \nu_2 = 2\,\nu_0$.

An experimental review of both methods follows in Section II. In Section III is a discussion of spin excitation by phonons at the resonance frequency and of the quadrupolar spin-lattice relaxation process. The important non-linear mechanisms which cause spin excitations are also discussed. In Section IV the experimental results are presented.

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[1]) Numbers in brackets refer to References, page 80.

Section II

The experimental details of both methods will be reviewed in this section. These experiments have been performed on GaAs in which the site symmetry is tetrahedral and all nuclei have spin $I = 3/2$. In a magnetic field of about 10.3 kilogauss the As^{75} nuclei have four equally spaced energy levels between which $\Delta^m = \pm 1$ transitions occur at $\nu_0 = 7.5$ MHz. The symmetry of the quadrupole interaction also allows $\Delta m = \pm 2$ transitions at $2\nu_0 = 15$ MHz. A standard Pulse nuclear induction system at 7.5 MHz is used to monitor the nuclear magnetization [6].

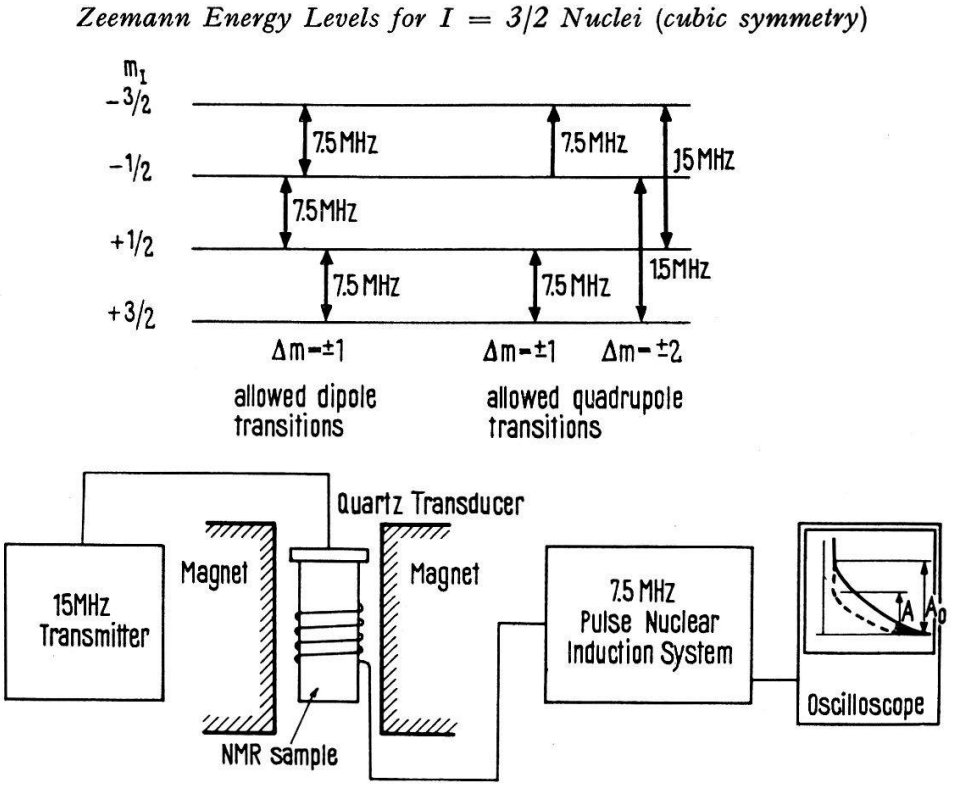

Figure 1

Zeeman energy level diagram and schematic diagram of the direct phonon-nuclear spin excitation system. Phonons are radiated into the NMR sample from a quartz transducer. Phonons at the Larmor frequency ν_0, or at $2\nu_0$ can cause spin transitions and reduce the signal amplitude from the Pulse Nuclear Induction System. It is usual to radiate phonons into the crystal at the $\Delta m = \pm 2$ transition frequency $2\nu_0$ in order to eliminate the possibility of causing saturation from dipolar transitions at ν_0.

For the usual method for phonon excitation of nuclear spin transitions, a transducer at the $\Delta m = \pm 2$ frequency is bonded to one surface of the sample. The transducer which radiates ultrasonic energy into the GaAs sample is an x-cut quartz crystal, one half acoustic wave length thick at the 15 MHz operation frequency. Phonons are radiated into the sample at the frequency of the voltage applied to the transducer. The phonons distort the lattice symmetry and cause a time varying electric field gradient. (The lattice displacement u is proportional to the voltage applied to the transducer). The spin transitions caused by resonant frequency phonons, reduce the nuclear magnetization. This saturation is detected as a reduction in the signal amplitude from the pulse nuclear induction apparatus.

For the non-linear method of exciting nuclear spin transitions phonons are radiated into the crystal simultaneously at two frequencies, neither of which can be resonant with the precessing nuclei. A 10 MHz and a 25 MHz transducer are bonded to opposite sides of a GaAs crystal that is otherwise in the same condition as described above. When the difference in the frequency of the voltage applied to the two transducers is adjusted to be resonant with the precessing nuclei, a saturation of the nuclear spin system is observed. In a similar way nuclear spin transitions have been induced with voltage applied at the respective frequencies of 5 and 10 MHz transducers bonded to the sample. In this case it is the sum frequency at 15 MHz of course, which is resonant with the precessing nuclei. Experimentally, the multiple phonon induced saturation is characterized by requiring more than two orders of magnitude greater voltage applied to the transducers, in order to produce the same saturation achieved with resonant frequency phonons radiated into the crystal. Both methods have in common however, that a proportionately greater voltage is required to saturate the Gallium than the Arsenic nuclei. This situation will be clarified in the next section.

Section III

In this section the different possible excitation mechanisms are discussed. The theory necessary to distinguish between the two most important mechanisms is also discussed.

Processes which can cause nuclear spin transitions are (A) magnetic field induced dipolar transitions, (B) direct phonon excitation by a process of second order in the quadrupole moment, (C) indirect phonon excitation by a Raman process, and (D) direct acoustic excitation by 15 MHz phonons, anharmonically produced by the lattice non-linearity. Process (A) is immediately eliminated since none of the power sources from which the transducers are supplied can produce electromagnetic radiation with the correct frequency to induce dipole transitions. Process (B) can be readily shown to be much smaller than process (C), so that it is only necessary to decide between process (C) and process (D).

The strongest mechanism for the excitation of these nuclear spin transitions is the anharmonic production of phonons at the resonant frequency of the precessing nuclei. Phonons at the 15 MHz resonant frequency are produced in the lattice because of the anharmonic nature of the crystal binding forces, and result in direct excitation of the nuclear spins [11]. However a Raman mechanism in which the nuclei are excited by an indirect or second order process is also possible. The Raman process does not require the presence in the lattice of phonons at the 15 MHz transition frequency. The Raman process is the important mechanism for spin-lattice relaxation of the nuclei in GaAs.

The previous multiple phonon experiments do not give sufficient information to allow the nuclear spin excitation mechanism to be identified. Although an experiment described in detail in reference [7] had shown process (D) to be dominant, this experiment is now known to be eronious because of a serious error. However the method which is the subject of this paper has resulted in the conclusive identification of the mechanism as process (D).

Phonons interact with the nuclear spins through the time varying electric field gradients they cause by lattice distortions. The Hamiltonian for the coupling of phonons to nuclei with quadrupole moments is the quadrupole moment operator

Q times a Taylor expansion of the electric field gradient E in powers of the lattice displacements $u_\alpha, u_\beta, \ldots$

$$H = Q\left[\gamma_0 E_0 + \gamma_1 \left(\frac{\partial E}{\partial x_\alpha}\right)_0 u_\alpha + \frac{\gamma^2}{2}\left(\frac{\partial^2 E}{\partial x_\alpha \partial x_\beta}\right)_0 u_\alpha u_\beta + \cdots\right]. \tag{1}$$

For clarity since we will be interested in discussing the ratio of this Hamiltonian between As^{75} and Ga^{69}, and since the lattice symmetry at both of these nuclear sites is the same, the subscripts labeling the nuclear sites in the crystal and the direction of displacement as well as the summations over these quantities have been omitted. The charge enhancement factors [8] γ_0, γ_1, and γ_2 multiplying the various derivatives of the electric field gradient account for the increased electric field gradient over that due to an ionic charge, because of distortion of the electron cloud by covalent bonding, charge overlap and polarization effects [9]. In the ionic model of GaAs the derivatives of the electric field gradient depend only upon geometrical lattice parameters which are the same for both Ga^{69} and As^{75}. The γ factors account for the physical difference between the ionic model and GaAs. For a given term in the Taylor expansion, separate γ factors are used to describe the difference in the field gradient at the Ga and As sites. These are phenomenological parameters which are determined from experiment. The electric field gradient tensor E combined with the quadrupole moment operator Q contain

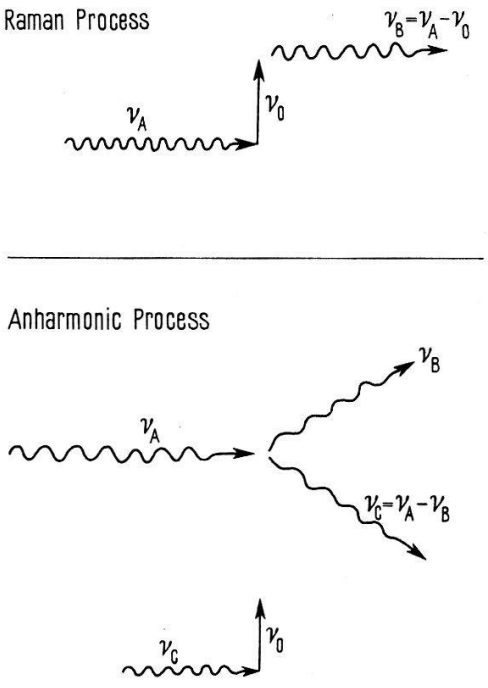

Figure 2

Diagrams of two interactions that cause nuclear spin transitions at ν_0 when phonons are in the lattice at the frequencies ν_A and ν_B. The anharmonic process involves two steps. Phonons at the transition frequency ν_0 are first produced by the interaction of phonons at the frequencies ν_A and ν_B. These anharmonically produced phonons at ν_0 then may interact with the nuclear spins to cause transitions. For the Raman process, the phonon at the transition frequency ν_0 need not be present in the lattice. The Raman process is due to the non-linearity of the electric field gradient. The Anharmonic process is due to non-linearity in the binding forces between the atoms. For both the Raman and Anharmonic processes, the selective annihilation of the phonon at ν_A to produce respectively a spin transition or phonon at ν_0 is stimulated by the presence in the lattice of intense phonon energy at the difference frequency ν_B.

off diagonal elements which describe $\Delta m = \pm 1$ transitions at the nuclear Larmor frequency ν_0 and $\Delta m = \pm 2$ transitions at $2\nu_0$. Henceforth we consider explicitly only $\Delta m = \pm 2$ transitions at $2\nu_0 \simeq 15$ MHz.

The first term in the Taylor expansion is static and of no interest in causing spin transitions. The next two terms depend upon time through the lattice displacements u_α and u_β. Spin transitions occur when these lattice displacements vary with the correct frequency. The linear term in u describes the interaction of a single phonon with the nuclear spin system. Phonons in the lattice at $2\nu_0$ excite direct transitions through this linear term. These direct spin excitations can be caused either by phonons radiated into the crystal from a transducer at $2\nu_0$, or by phonons at this frequency created through the lattice non-linearity.

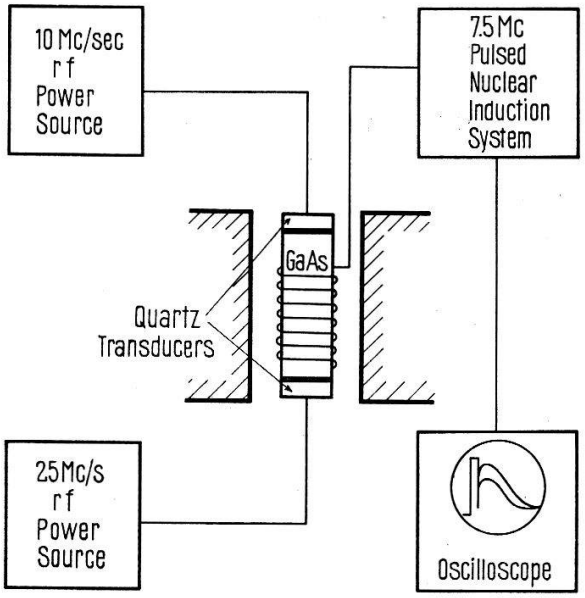

Figure 3

Schematic diagram for exciting non-linearly induced nuclear spin transitions. Transducers, whose half-wave length thickness corresponds to the frequency of their respective power sources, are bonded to opposite sides of the sample. The nuclear induction system measures a decrease in signal amplitude, when the difference in the frequency of the power applied to the transducers is adjusted to be resonant with the precessing nuclei.

The term quadratic in u describes the interaction of two phonons with the nuclear spin. This is a Raman type of interaction and takes place when the sum or difference frequency of the phonons is resonant with the precessing nuclei. It is through this quadratic term that the process of spin-lattice relaxation in GaAs takes place [8] [11]. It is to be observed that the charge enhancement factor γ_2 is involved for the spin-lattice relaxation, and γ_2 is involved if the multiple phonon-spin excitation mechanism is a Raman process. However if the 10 MHz and 25 MHz phonons are converted into 15 MHz phonons by the lattice non-linearity, then these 15 MHz phonons interact directly with the spin system through the linear term involving a γ_1. It will be shown upon comparing the excitation strengths of Ga^{69} and As^{75}, one obtains a result depending upon the ratio of the γ_1's for these two nuclei, indicating that the mechanism is due to lattice non-linearity.

In a volume element small with respect to the phonon wave length, the ratio of the nuclear magnetization M to M_0, the equilibrium magnetization with no phonon energy radiated into the sample, is

$$\frac{M}{M_0} = \frac{A}{A_0} = \left[1 + \frac{8}{5} PT_1\right]^{-1} \tag{2}$$

for the spin $I = 3/2$ nuclei in GaAs [12]. A is the nuclear induction signal amplitude, P is the phonon induced transition probability and T_1 is the spin-lattice relaxation time. For a constant value of the product PT_1 the same signal amplitude ratio A/A_0 is obtained for both Ga^{69} and As^{75}.

The expression for the spin-lattice relaxation time is found in reference 8 and 11. We write below the functional dependence suitable for our purpose

$$T_1 = [Q^2 \gamma_2^2 E(T)^2 f(I)]^{-1}. \tag{3}$$

$f(I)$, a function of the nuclear spin, and $E(T)$, the geometrical expression for the electric field gradient which depends upon the temperature T and lattice constants, are functions which are the same for all nuclei in GaAs.

The transition probability P is

$$P = \frac{1}{\hbar^2} \langle H \rangle^2 g(\nu), \tag{4}$$

where $g(\nu)$ is the line shape function for the phonon induced spin transition. The matrix element $\langle H \rangle$ contains the term from the Hamiltonian (Eqn. 1) corresponding to the excitation process.

Since we compare the product PT_1 at the same temperature, for nuclei with the same spin in the same site symmetry, these uninteresting parameters which do not change for the different nuclear species, are lumped into the constant K.

$$PT_1 = \frac{1/\hbar^2 \langle H \rangle^2 g(\nu)}{Q^2 \gamma_2^2 E(T)^2 f(I)} = \frac{\langle H \rangle^2 g(\nu)}{Q^2 \gamma_2^2} K. \tag{5}$$

The charge enhancement factor and the field gradient term in the transition probability, depend upon the type of excitation process involved. If the excitation is Raman, the charge enhancement factor in the numerator is γ_2^2 which cancels with the γ_2^2 from the T_1 to yield a product PT_1 that is independent upon the nuclear species in GaAs. (Ga^{69} and As^{75} have approximately the same line shape factors). In other words, if the mechanism is Raman, the transducer voltage required for a given saturation for As^{75} will produce the same saturation for Ga^{69}.

However if the mechanism is the anharmonic production of 15 MHz phonons, the charge enhancement factor would be γ_1. For this case the ratio of PT_1 between Ga^{69} and As^{75} is

$$\frac{(PT_1)_{69}}{(PT_1)_{75}} = \frac{[Q^2 \gamma_1^2 (\partial E/\partial x_\alpha)_0^2 u_\alpha^2 g(\nu) T_1]_{69}}{[Q^2 \gamma_1^2 (\partial E/\partial x_\alpha)_0^2 u_\alpha^2 g(\nu) T_1]_{75}}. \tag{6}$$

The $(\partial E/\partial x_\alpha)_0$ for Ga^{69} and As^{75} cancel since these factors depend only upon lattice geometry and it is the γ_1 factors which describe any differences in the electric field gradient between the respective sites.

$$\frac{(PT_1)_{69}}{(PT_1)_{75}} = \frac{(Q^2 \gamma_1^2 g(\nu) T_1 u_\alpha^2)_{69}}{(Q^2 \gamma_1^2 g(\nu) T_1 u_\alpha^2)_{75}}. \tag{7}$$

The u_α^2 is proportional to the phonon energy present in the lattice at $2\nu_0$. Hence for the anharmonic production of 15 MHz phonons u_α^2 is proportional to the product of the phonon energies at the 10 MHz and 25 MHz frequencies.

The exact value of this ratio depends upon the orientation of the GaAs crystalline axis along the magnetic field. The line width is observed to considerably broaden for small deviations of the $\{100\}$ direction from being parallel to the magnetic field. This is apparently due to a preferential distribution of lattice imperfections, which results in static field gradients oriented along the $\{111\}$ axis [13]. There is also the possibility that the ratio of the γ_1's depends upon the crystal orientation in the magnetic field. However from previous measurements of the γ_1 ratio [14], a difference in the excitation sensitivity would be expected for any orientation.

The exact excitation sensitivity ratio for the two nuclei may be obtained by comparing the nuclear spin saturation from the anharmonic process, with the saturation from phonons at $2\nu_0$ radiated directly into the lattice and with the same crystal orientation. For the direct saturation, equation 7 is also valid. For the direct saturation u_α^2 is proportional to the square of the voltage applied to the transducer $(V_{15})^2$. For the anharmonic mechanism u_α^2 is proportional to $(V_{10}\,V_{25})^2$, where V_{10} and V_{25} are respectively the voltages applied to the 10 MHz and 25 MHz transducers.

$$\frac{(P\,T_1)_{69}}{(P\,T_1)_{75}} = \frac{[Q^2\,\gamma_1^2\,g(\nu)\;T_1\,(V_{10}\,V_{25})^2]_{69}}{[Q^2\,\gamma_1^2\,g(\nu)\;T_1\,(V_{10}\,V_{25})^2]_{75}} \tag{8a}$$

$$= \frac{[Q^2\,\gamma_1^2\,g(\nu)\;T_1(V_{15})^2]_{69}}{[Q^2\,\gamma_1^2\,g(\nu)\;T_1(V_{15})^2]_{75}}\,. \tag{8b}$$

For the same saturation, the Ga^{69}-As^{75} voltage ratio term should be the same for both the direct saturation (Equation 8b), and for the non-linear saturation (Equation 8a), if the non-linear saturation is due to the anharmonic production of phonons at $2\nu_0$. In the next section, data is presented which shows this to be the case.

Section IV

The ratio of the nuclear induction signal amplitude A to A_0, the equilibrium signal amplitude for no phonon energy radiated into the crystal, is plotted as a function of an abscissa that is proportional to the phonon energy in the lattice at $2\nu_0$. All of the data was taken at liquid nitrogen temperature in order to obtain conveniently long relaxation times. The sample was a single crystal of insulating GaAs oriented with the $\{100\}$ direction approximately along the magnetic field.

The actual frequencies used for these measurements were chosen to correspond to the frequencies of maximum power output from the 10 MHz and 25 MHz transducers. These correspond to the rather broad mechanical resonances centered at 10.500 MHz and 25.364 MHz respectively. The difference frequency ($2\nu_0 = 14.864$ MHz) was also applied to the 15 MHz transducer without regard for its mechanical resonance since sufficient power to obtain direct saturation was not a problem. The magnetic field was adjusted for a Larmor frequency ν_0 at 7.432 MHz and was held constant with the aid of a separate proton-nuclear magnetic resonance system. The different frequencies were held constant with the aid of a frequency counter.

Between the data taken for figures (4) and (5), it was, of course, necessary to remove the sample from the magnetic field in order to replace the 15 MHz transducer

with the 10 and 25 MHz transducers. As a check that the orientation of the crystal with respect to the magnetic field had not changed, power at 14.864 MHz was applied to the 10 and 25 MHz transducers. Sufficient phonon energy was obtained at 14.864 MHz to obtain saturation of the Ga^{69} and As^{75} in agreement with that presented in figures (4) and (5).

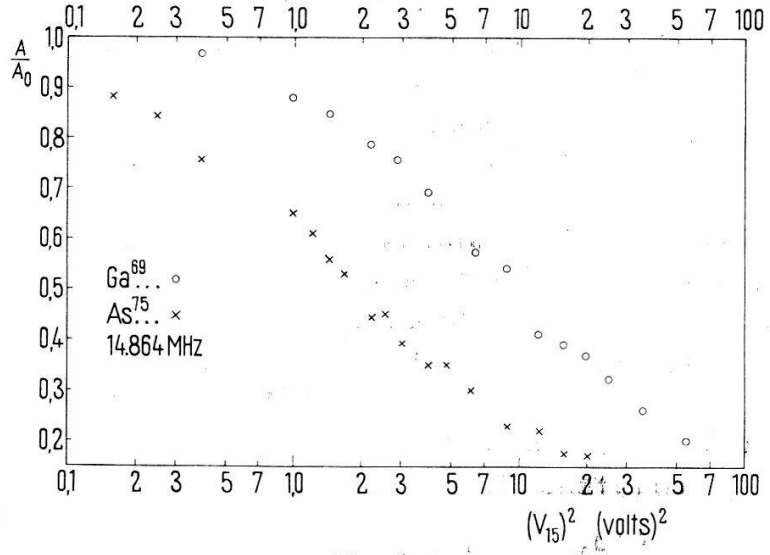

Figure 4

Saturation curves for Ga^{69} and As^{75} vs. the squared voltage applied at 14.864 MHz to a 15 MHz transducer. Conditions are maintained so that a given voltage applied to the transducer produces the same phonon energy density in the crystal for the saturation of both nuclei.

A theoretical curve has not been drawn through the data since its form depends upon the knowledge of the phonon energy distribution within the sample. Because of scattering and poor sample geometry with respect to phonon wave length, which leads to the excitation of complex vibrational modes, the exact phonon energy distribution

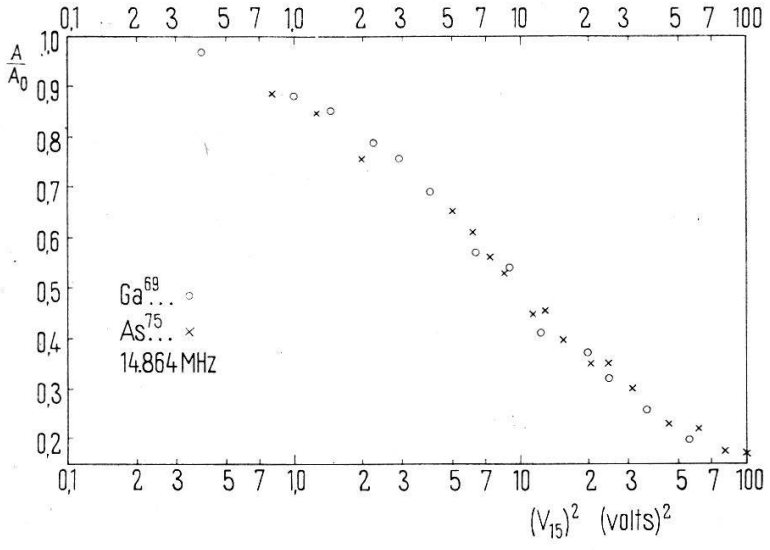

Figure 5

The As^{75} voltage squared coordination of the data in the previous Figure have been multiplied by a factor of 5 in order to bring the As data into coincidence with the Ga^{69} data.

would be difficult to determine. That the distribution is, however, the same for both the direct and the non-linear nuclear spin excitation, is quite likely for two reasons. First, momentum and energy conservation require that the anharmonically produced phonon at $2\,\nu_0$ have a direction parallel to the phonons from the 10 and 25 MHz transducers. These phonons are therefore produced with the same geometry as the phonons which are radiated into the sample at $2\,\nu_0$ for the direct nuclear spin excitation experiment. Second, within experimental error, the saturation curves for direct spin excitation and non-linear spin excitation have the same form.

The difference in the direct excitation sensitivity between Ga^{69} and As^{75} is about a factor of 5 in phonon energy. When the abscissa coordinates for As^{75} in Figure 4 are multiplied by a factor of 5 the Ga and As data follow the same saturation curve to a very good approximation, as can be seen from figure 5.

The data for the non-linear nuclear spin excitation of Ga^{69} and As^{75} is presented in Figure 6. If the abscissa coordinates of the Ga^{69} data are divided by 4.7, the Ga and As follow the same saturation curve as can be seen in Figure 7.

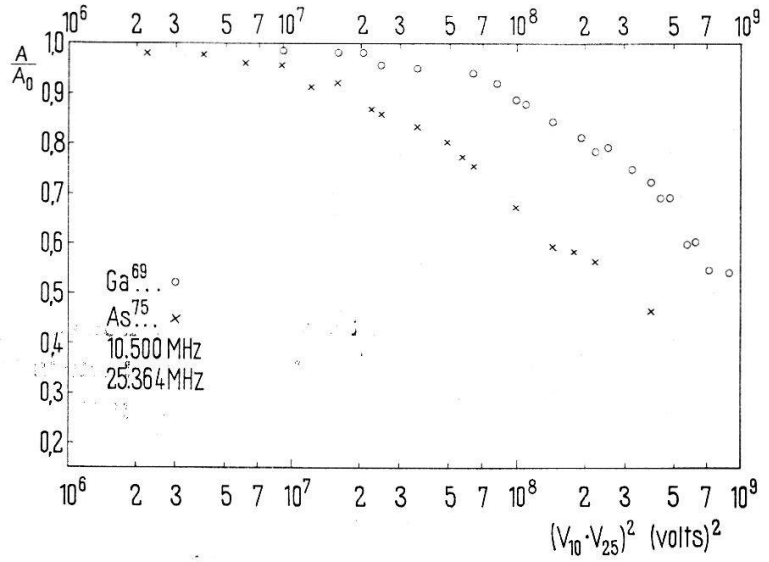

Figure 6

Saturation curves for Ga^{69} and As^{75} vs. the product of the squared voltages applied to the 10 MHz and 25 MHz transducers.

The relatively good agreement between the factors 5 and 4.7 for the direct and non-linear saturation data, is conclusive evidence that the non-linear nuclear spin excitation mechanism is through the anharmonic production of difference frequency phonons at $2\,\nu_0$. The maximum excitation sensitivity difference, if the non-linear mechanism were due to the Raman process, would be about 30% instead of the 470% observed. The factor of 30% would come from the difference in the line shape factors.

In conclusion, it has been shown that the nuclear spin transitions excited by intense phonon energy applied at two separate frequencies, whose difference frequency is $2\,\nu_0$, is due to the anharmonic production of transition frequency phonons. The significance of this result is that it shows that the nuclear spin system can serve as a detector of anharmonically produced (either coherent or incoherent) phonons. This

allows the nuclei to be used to measure the anharmonic elastic coefficients of suitable crystals. Some measurements of the anharmonic coupling coefficients in GaAs have already been made and will be reported in a future communication.

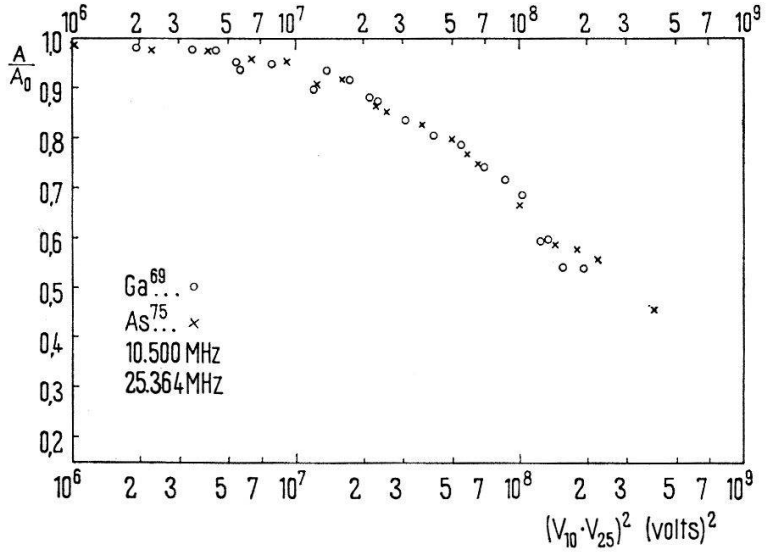

Figure 7

The abscissa coordinates of the Ga^{69} non-linear saturation data of the previous Figure have been divided by a factor of 4.7 in order to bring them into coincidence with As^{75} data.

I wish to thank Prof. E. BRUN for his very helpful criticism of this work and to thank Profs. O. LEIFSON and F. WALDNER and Dr. W. PROCTOR for stimulating discussions. The help of Mr. E. HUNDT with some of the measurements and the financial support of the Schweizerischer Nationalfonds is gratefully acknowledged.

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