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PRECISE MEASUREMENT OF CHARGED DEFECTS IN III-V COMPOUNDS (2)

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Introduction

The main objective of this research is to obtain a calibration of a low concentration of charged defects in some III-V semiconducting compounds. The experimental technique being used is nuclear magnetic resonance (NMR), and the objective is to be attained through a thorough examination of the properties of the NMR lines of the nuclei in the III-V compounds.

Understanding the properties of the NMR lines, and how they are influenced by the presence of charged defects, requires both theoretical and experimental exploration. This report is thus divided into three sections: I. Theory, II. Experiment, and III. Conclusions.

I

I. THEORY

The sensitivity to defects achieved in this work will depend on a detailed knowledge of the magnetic resonance line shape. The best calculation of the magnetic resonance line shape in solids was done by Lowe and Norberg(1). However Abragam(2) has proposed a two parameter shape function that reproduces the observed shapes as well as the Lowe-Norberg theory and is much simpler in form. More recently Betsuyaku(3) has extended the Lowe-Norberg calculation to include higher order terms in their expansion. This extension removes the agreement between the theory and experiment. Thus this fundamental problem remains in unsatisfactory shape.

A new approach to the problem is needed. It is suggested that a combination of "single site approximations" and the "coherent potential approximation"(4) may prove useful.

In order to apply the methods suggested above, a knowledge of the normal modes, or at least a set of almost normal modes, of the spin system is needed. A preliminary and still incomplete study of these modes is described below.

The secular part of the dipole-dipole Hamiltonian $\mathcal{H}$ coupling a system of identical spins is

$$\mathcal{H}=\sum_{\vec{\ell},\vec{\ell}'}{}' a_{\vec{\ell}\vec{\ell}'}\left(\vec{I}^{\vec{\ell}}\cdot\vec{I}^{\vec{\ell}'}-3I_z^{\vec{\ell}}I_z^{\vec{\ell}'}\right)=\sum_{\vec{\ell},\vec{\ell}'}{}'\vec{I}^{\vec{\ell}}\cdot\underset{\sim}{A}_{\vec{\ell}\vec{\ell}'}\cdot I_z^{\vec{\ell}'}, \qquad (1)$$

where $a_{\vec{\ell}\vec{\ell}'}\equiv-\frac{\gamma^2\hbar^2}{4}\left(1-3\cos^2\theta_{\vec{\ell}\vec{\ell}'}\right)\left|\vec{\ell}'-\vec{\ell}\right|^{-3}$

γ is the magnetogyric ratio for the spins,

$\hbar$ is Planck's constant,

$\vec{\ell}$ is the lattice vector designating a nuclear position,

$\cos\theta_{\vec{\ell}\vec{\ell}'} = \frac{\vec{\ell}'-\vec{\ell}}{|\vec{\ell}'-\vec{\ell}|}\cdot\hat{H}_0$

$\vec{H}_0$ is the external d.c. magnetic field,

$\vec{I}^{\vec{\ell}}$ is the spin operator of the $\vec{\ell}$ nucleus, and

$$\underset{\sim}{A}_{\vec{\ell}\vec{\ell}'} \equiv a_{\vec{\ell}\vec{\ell}'}\left(\hat{x}\hat{x}+\hat{y}\hat{y}-2\hat{z}\hat{z}\right) = \underset{\sim}{A}_{\vec{\ell}'\vec{\ell}}\,. \tag{2}$$

The objective is to find a normal modes transformation that diagonalizes this Hamiltonian.

Try the transformation

$$\vec{I}^{\vec{\ell}} = \frac{1}{\sqrt{N}}\sum_{\vec{k},\beta} q_{\vec{k}\beta}\,\hat{e}_{\vec{k}\beta}\,e^{i\vec{k}\cdot\vec{\ell}} \tag{3}$$

where N is the number of spins in the system, including periodic boundary conditions, $\vec{k}$ is a reciprocal lattice vector which ranges over the first Brillouin zone, and β is a polarization index which takes on three possible values. As the calculation proceeds it will become obvious how $q_{\vec{k}\beta}$ and $\hat{e}_{\vec{k}\beta}$ are to be found.

Substitute Eq. (3) into Eq. (1). Then one finds

$$\mathcal{H} = \frac{1}{N}\sum_{\substack{\vec{k},\beta\\ \vec{k}',\beta'}} q_{\vec{k}\beta}\,q_{\vec{k}'\beta'}\,\hat{e}_{\vec{k}\beta}\cdot\underset{\sim}{\mathcal{A}}(\vec{k}')\cdot\hat{e}_{\vec{k}'\beta'}\,e^{i(\vec{k}+\vec{k}')\cdot\vec{\ell}}\,, \tag{4}$$

where

$$\underset{\sim}{\mathcal{A}}(\vec{k}') \equiv \sum_{\vec{l}'}{}' \underset{\sim}{A}_{\vec{l}\vec{l}'} e^{i\vec{k}'\cdot(\vec{l}'-\vec{l})} = \underset{\sim}{\mathcal{A}}(-\vec{k}') .$$

Choose the $\hat{e}_{\vec{k}'\beta'}$ to be the eigenvalues of the diadic $\underset{\sim}{\mathcal{A}}(\vec{k}')$, i.e.,

$$\underset{\sim}{\mathcal{A}}(\vec{k}')\cdot\hat{e}_{\vec{k}'\beta'} = \hbar\,\omega_{\vec{k}'\beta'}\,\hat{e}_{\vec{k}'\beta'} . \tag{5}$$

Since $\underset{\sim}{\mathcal{A}}(\vec{k}') = \underset{\sim}{\mathcal{A}}(-\vec{k}')$, we know that $\hat{e}_{\vec{k}'\beta'} = \hat{e}_{-\vec{k}'\beta'}$ and $\omega_{\vec{k}'\beta'} = \omega_{-\vec{k}'\beta'}$. $\underset{\sim}{\mathcal{A}}$ is a diagonal diadic, hence its eigenvalues and eigenvectors are trivial to find. This general formalism is presented in case it ever becomes useful to use this method on more complex spin Hamiltonians, e.g. the full dipole-dipole interaction. The eigenvectors of $\underset{\sim}{\mathcal{A}}(\vec{k})$ are

$$\hat{e}_{\vec{k}\beta} = \hat{\beta} \quad , \quad \hat{\beta} = \hat{x}, \hat{y}, \hat{z} , \tag{6}$$

and the corresponding eigenvalues are

$$\omega_{\vec{k}x} = \omega_{\vec{k}y} = -\tfrac{1}{2}\omega_{\vec{k}z} = \frac{1}{\hbar}\sum_{\vec{l}'} a_{\vec{l}\vec{l}'}\, e^{i\vec{k}\cdot(\vec{l}'-\vec{l})} \tag{7}$$

$$= -\frac{\gamma^2\hbar}{4}\sum_{\vec{l}}{}' \frac{(1-3\cos^2\theta_l)}{l^3} e^{i\vec{k}\cdot\vec{l}} = -\frac{\gamma^2\hbar}{8}\sum_{\vec{l}} \frac{(1-3\cos^2\theta_l)}{l^3}\cos(\vec{k}\cdot\vec{l}),$$

with $\cos\theta_l = \hat{l}\cdot\hat{H}_0$. Note that $\omega_{0x} = 0$ for a crystal with a center of symmetry. However we shall see that $\omega_{\vec{k}x}$ is almost discontinuous near $k=0$ and, for $k \sim 1/N^{1/3}$, $\omega_{\vec{k}x}$ is not small. An approximate expression for $\omega_{\vec{k}x}$ is developed in Appendix I.

Now return to the diagonalization of $\mathcal{H}$. Inserting Eqs. (5) and (6) into Eq. (4) converts it to the form

$$\mathcal{H} = \frac{1}{N} \sum_{\substack{\vec{\ell} \\ \vec{k},\vec{k}',\beta,\beta'}}' q_{\vec{k}\beta}\, q_{\vec{k}'\beta'}\, \hat{\beta}\cdot \hbar\omega_{\vec{k}'\beta'}\, \hat{\beta}'\, e^{i\vec{\ell}\cdot(\vec{k}+\vec{k}')} . \tag{8}$$

The sum over $\vec{\ell}$ is $\sum'_{\vec{\ell}} e^{i\vec{\ell}\cdot(\vec{k}+\vec{k}')} = \delta_{\vec{k},-\vec{k}'}$, a Kronecker delta of $\vec{k}$ and $\vec{k}'$. Then, since $\hat{\beta}\cdot\hat{\beta}' = \delta_{\beta\beta'}$, the $\mathcal{H}$ becomes

$$\mathcal{H} = \sum_{\vec{k},\beta}' \hbar\omega_{\vec{k}\beta}\, q_{\vec{k}\beta}\, q_{-\vec{k}\beta} . \tag{9}$$

Since $\vec{\mathrm{I}}^{\vec{\ell}}$ is a Hermitean operator, Eq. (3) gives us

$$\begin{aligned} \sum_{\vec{k}\beta}' q^{\dagger}_{\vec{k}\beta}\, \hat{e}_{\vec{k}\beta}\, e^{i\vec{k}\cdot\vec{\ell}} &= \sum_{\vec{k}\beta}' q_{\vec{k}\beta}\, \hat{e}_{\vec{k}\beta}\, e^{i\vec{k}\cdot\vec{\ell}} \\ &= \sum_{\vec{k}\beta}' q_{-\vec{k}\beta}\, \hat{e}_{\vec{k}\beta}\, e^{i\vec{k}\cdot\vec{\ell}} , \end{aligned} \tag{10}$$

where the last equality is reached by substituting $-\vec{k}$ for $\vec{k}$ everywhere in the term on the left and using the fact that $\hat{e}_{\vec{k}\beta} = \hat{e}_{-\vec{k}\beta}$. The equality of the last two terms in Eq. (10) implies that

$$q^{\dagger}_{-\vec{k}\beta} = q_{\vec{k}\beta} , \tag{11}$$

since the expressions must hold for arbitrary $\vec{\ell}$. Eq. (11) can be used to write Eq. (9) in the form

$$\mathcal{H} = \sum_{\vec{k}\beta}' \hbar\omega_{\vec{k}\beta}\, q_{\vec{k}\beta}\, q^{\dagger}_{\vec{k}\beta} . \tag{12}$$

In order to complete this discussion, we now examine the commutation relations among the $q_{\vec{k}\beta}$ and $q^{+}_{\vec{k}\beta}$ operators. First the inverse transform of Eq. (3) yields

$$q_{\vec{k}\beta} = \frac{1}{\sqrt{N}} \sum_{\vec{l}} \vec{I}^{\vec{l}} \cdot \hat{\beta}\, e^{-i\vec{k}\cdot\vec{l}} . \tag{13}$$

Then the commutator between $q_{\vec{k}\beta}$ and $q_{\vec{k}'\beta'}$ is

$$[q_{\vec{k}\beta}, q_{\vec{k}'\beta'}] = \frac{1}{N} \sum_{\vec{l},\vec{l}'} [\vec{I}^{\vec{l}} \cdot \hat{\beta}, \vec{I}^{\vec{l}'} \cdot \hat{\beta}']\, e^{-i(\vec{k}\cdot\vec{l}+\vec{k}'\cdot\vec{l}')} ,$$

but $$[\vec{I}^{\vec{l}} \cdot \hat{\beta}, \vec{I}^{\vec{l}'} \cdot \hat{\beta}'] = [\vec{I}^{\vec{l}} \cdot \hat{\beta}, \vec{I}^{\vec{l}} \cdot \hat{\beta}']\, \delta_{\vec{l}\vec{l}'} ,$$

so

$$[q_{\vec{k}\beta}, q_{\vec{k}'\beta'}] = \frac{1}{N} \sum_{\vec{l}} [\vec{I}^{\vec{l}} \cdot \hat{\beta}, \vec{I}^{\vec{l}} \cdot \hat{\beta}']\, e^{-i(\vec{k}+\vec{k}')\cdot\vec{l}} . \tag{14}$$

Examine the special cases $\beta, \beta' = x, y, z$:

$$[q_{\vec{k}\beta}, q_{\vec{k}'\beta}] = 0, \tag{15}$$

$$[q_{\vec{k}x}, q_{\vec{k}'y}] = \frac{1}{N} \sum_{\vec{l}} i I_z^{\vec{l}}\, e^{-i(\vec{k}+\vec{k}')\cdot\vec{l}} = \frac{i}{\sqrt{N}} q_{\vec{k}+\vec{k}', z} , \tag{16}$$

$$[q_{\vec{k}y}, q_{\vec{k}'z}] = \frac{i}{\sqrt{N}} q_{\vec{k}+\vec{k}', x} , \tag{17}$$

$$[q_{\vec{k}z}, q_{\vec{k}'x}] = \frac{i}{\sqrt{N}} q_{\vec{k}+\vec{k}', y} . \tag{18}$$

Similarly, one finds

$$[q_{\mathbf{k}\beta}, q^{\dagger}_{\mathbf{k}'\beta}] = 0 \;, \qquad (19)$$

$$[q_{\mathbf{k}x}, q^{\dagger}_{\mathbf{k}y}] = \frac{i}{\sqrt{N}}\, q_{\mathbf{k}-\mathbf{k}',z} \;, \qquad (20)$$

$$[q^{\dagger}_{\mathbf{k}\beta}, q^{\dagger}_{\mathbf{k}'\beta}] = 0 \,, \qquad (21)$$

$$[q^{\dagger}_{\mathbf{k}x}, q^{\dagger}_{\mathbf{k}'y}] = \frac{i}{\sqrt{N}}\, q^{\dagger}_{\mathbf{k}+\mathbf{k}',z} \;, \qquad (22)$$

plus cyclic permutations of Eqs. (20) and (22).

Using Eq. (19), Eq. (12) can be rewritten in a familiar form:

$$\mathcal{H} = \sum_{\mathbf{k}\beta}{}' \hbar\,\omega_{\mathbf{k}\beta}\, q^{\dagger}_{\mathbf{k}\beta}\, q_{\mathbf{k}\beta} \;. \qquad (23)$$

Although this Hamiltonian is written as a sum of one "particle" operators, the operators corresponding to different polarizations β do not commute. Hence the Hamiltonian is not yet diagonal. Operators for different $\mathbf{k}$ but the same polarization do commute. There are a few other commutation relations and theorems which can be derived, but so far we have been unable to find another transformation that completes the diagonalization of the Hamiltonian.

For example, the net magnetization $\mathcal{M}_z$ can be expressed in terms of the $q_{\mathbf{k}\beta}$ as

$$\mathcal{M}_z = \sum_{\vec{l}}{}' \hbar\gamma I_z^{\vec{l}} = \hbar\gamma\sqrt{N}\, q_{0z} \;. \qquad (24)$$

Other commutation relations that prove to be useful are (in these expressions the arrow is left off the vectors $\vec{k}$, $\vec{k}'$):

$$[q^\dagger_{kx} q_{kx}, q_{k'z}] = \frac{-i}{\sqrt{N}} \left(q^\dagger_{k-k',y} q_{kx} + q^\dagger_{kx} q_{k+k',y} \right) \tag{25}$$

$$[q^\dagger_{ky} q_{ky}, q_{k'z}] = \frac{i}{\sqrt{N}} \left(q^\dagger_{k-k',x} q_{ky} + q^\dagger_{ky} q_{k+k',x} \right) \tag{26}$$

$$[q^\dagger_{kx} q_{kx}, q^\dagger_{k'z}] = \frac{-i}{\sqrt{N}} \left(q^\dagger_{k+k',y} q_{kx} + q^\dagger_{kx} q_{k-k',y} \right) \tag{27}$$

$$[q^\dagger_{ky} q_{ky}, q^\dagger_{k'z}] = \frac{i}{\sqrt{N}} \left(q^\dagger_{k+k',x} q_{ky} + q^\dagger_{ky} q_{k-k',x} \right) \tag{28}$$

$$\begin{aligned}[q^\dagger_{kx} q_{kx}, q^\dagger_{k'z} q_{k'z}] = \frac{-i}{\sqrt{N}} \Big(& q^\dagger_{k'z} q^\dagger_{k-k'y} q_{kx} + q^\dagger_{k'z} q_{kx} q_{k+k',y} \\ & + q^\dagger_{k+k',y} q_{kx} q_{k'z} + q^\dagger_{ky} q_{k-k',x} q_{k'z} \Big)\end{aligned} \tag{29}$$

$$\begin{aligned}[q^\dagger_{ky} q_{ky}, q^\dagger_{k'z} q_{k'z}] = \frac{i}{\sqrt{N}} \Big(& q^\dagger_{k'z} q^\dagger_{k-k',x} q_{ky} + q^\dagger_{k'z} q^\dagger_{ky} q_{k+k',x} \\ & + q^\dagger_{k+k',x} q_{ky} q_{k'z} + q^\dagger_{ky} q_{k-k',x} q_{k'z} \Big)\end{aligned} \tag{30}$$

From Eqs. (25), (26), and the fact that $\omega_{kx} = \omega_{ky} = -\frac{1}{2}\omega_{kz}$, it is easy to show that

$$[q_{0z}, \mathcal{H}] = 0 \tag{31}$$

or equivalently from Eq. (24)

$$[\mathcal{M}_z, \mathcal{H}] = 0 \tag{32}$$

Eq. (32) is not too surprising since that is the condition used to pick the secular part of the full dipole-dipole Hamiltonian.

If $\mathcal{H}$ can be completely diagonalized then the Lowe-Norberg problem can be solved exactly. However, since this Hamiltonian is a generalization of the Ising model which has yet to be solved, it seems unlikely that we shall succeed. It does seem worth a bit more effort. The fact that the commutation relations, Eqs. (15)-(22), involve a $1/\sqrt{N}$ factor may prove to be useful in some expansions. However care must be used since some $q_{\vec{k}\beta}$'s may be of order $\sqrt{N}$. For example, for a system of spin 1/2 particles in the ferromagnetic state with all spins up $|\uparrow\rangle$

$$\langle\uparrow| q_{kz} |\uparrow\rangle = \frac{1}{\sqrt{N}} \langle\uparrow| \sum_{\vec{l}} I_z^{\vec{l}} e^{i\vec{k}\cdot\vec{l}} |\uparrow\rangle$$

$$= \frac{1}{2} \frac{1}{\sqrt{N}} \sum_{\vec{l}} e^{i\vec{k}\cdot\vec{l}} = \frac{\sqrt{N}}{2} \delta_{\vec{k},0} ,$$

the $k = 0$ matrix element is large while all the others are zero. For states with nearly random spin orientations, the matrix elements of the $q_{\vec{k}\beta}$'s are probably mostly of order $1/\sqrt{N}$, but this hasn't been proven.

A good deal remains to be done on this subject so this work will continue. We shall also try to extend these ideas to help analyze the Waugh(4) type experiments.

II. EXPERIMENT

E. H. Rhoderick has investigated the nuclear magnetic resonance of doped and undoped indium antimonide and gallium arsenide.[5] He found that the intensity of the resonance absorption derivative decreased with increasing concentrations of impurity. In fact, his data show a sharp decrease in the intensity of the resonance as the impurity concentration increases up to 10^{18} cm^{-3}. Concentrations larger than $10^{18} cm^{-3}$ serve to further reduce the intensity, but at a much slower rate.

The explanation for this behavior is as follows. In the pure compound the resonance line is broadened significantly mostly by the magnetic dipole-dipole interaction. The resonance line in a perfect crystal is not broadened by the quadrupole interaction because the lattice has cubic symmetry and each atomic site has zero electric field gradient. An impurity destroys the cubic symmetry in its neighborhood, and broadens the resonance line through the quadrupole interaction. Since the quadrupole moments of each of these nuclei are large, the satellite transitions ($3/2 \rightarrow 1/2$, etc.) are split far from the resonance line and do not contribute to the detected resonance. The initial sharp decrease in intensity is thus due to the loss of the satellites from the resonance line. The gradual decrease in intensity observed by increasing impurity concentrations greater than $10^{18} cm^{-3}$ is due to a broadening of the central component (the $1/2 \rightarrow 1/2$ transition) by the quadrupole interaction. This broadening is always present, but its effect can be distinguished only when the central component alone is detected.

Among the other conclusions that Rhoderick draws from his data is that the antishielding factor necessary to explain the sharp decrease in intensity is very large, on the order of 10^3. We have used Rhoderick's data to make an independent calculation of the strength of the quadrupole interaction, and we find that it is 2000 times stronger than predicted by a simple point charge defect model.

Our calculation consists of assuming that the impurity atom will assume a net charge at its lattice site of γe, where γ is a dimensionless parameter describing the strength of the interaction. This produces an electric field gradient at the sites of nearby nuclei. In particular, a nucleus a distance r away from the impurity will have satellite lines shifted by an amount

$$f_s = \frac{\gamma e^2 Q}{4hr^3}(3\cos^2\theta - 1)\left(\frac{2\epsilon+3}{5\epsilon}\right),$$

where ϵ is the dielectric constant, eQ is the electric quadrupole moment of the nucleus, and θ is the angle between the vector from the impurity to the nucleus and the static magnetic field direction. If f_s is small, the satellite shift will serve only to broaden the resonance line; but a large f_s corresponds to loss of the satellite components of the resonance. In this calculation of the strength of the quadrupole interaction we choose a frequency f such that if $f_s < f$ for a given nucleus, then we may still see its satellite contributions; but if $f_s \geq f$, it will be split far enough that we cannot detect it.

In order to calculate the total number of nuclei that contribute only the $(-1/2 \rightarrow 1/2)$ component to the resonance line we need to calculate the volume about each impurity in which $f_s \geq f$ for every Ga^{69} atom. This volume is found to be

$$V = \frac{16\pi\sqrt{3}}{27}\left(\frac{\gamma e^2 Q}{4hf_s}\right)\left(\frac{2\epsilon+3}{5\epsilon}\right).$$

Then the number of nuclei within the volume is $N = n_o V$, where n_o is the atomic density of Ga^{69}. Since, as we shall see,this interaction is very strong, then the volume V is large and we are justified in using a continuum model for the lattice.

The intensity of the resonance line is proportional to the density of Ga^{69} atoms, n_o , within the specimen; but the intensity of the resonance when all the satellites are shifted beyond detection must be proportional to $.4\ n_o$. If the interpretation of the intensity behavior is correct, then the linear decrease of intensity with increasing impurity concentration should extrapolate back at zero concentration to the intensity of an unbroadened central component, which is $.4n_o$. Actually, Rhoderick's data extrapolate back to .6 of initial intensity, indicating that in his "pure" crystal not all the satellites were present. Let n' represent the atomic density which at zero impurity concentration contributes only the central component. Then with zero impurity concentration the intensity may be written

$$I = K(n_o - .6n') ,$$

where K is the normalization constant. Rhoderick normalizes this intensity to unity. The extrapolation to zero concentration yields

$$.6 = .6K(n_o - .6n') = .4Kn_o ,$$

or

$$n_o - .6n' = \frac{2}{3}n_o \quad , \quad \text{and} \quad K = \frac{3}{2n_o}$$

Rhoderick's "pure" sample contained only 4/9 of the satellites. We can now write the intensity of the resonance at a given impurity concentration, C,

$$I = \frac{3}{2n_o}(n_o - .6n' - .6n_oVC),$$

and by differentiation,

$$\frac{dI}{dC} = \left(\frac{2\pi\sqrt{3}}{15}\right)\frac{\gamma e^2 Q}{hf}\left(\frac{2\epsilon+3}{5\epsilon}\right)$$

We use the value of dI/dC from Rhoderick's data and the value of 3 KHz for f_s, which is half the total width of the Ga^{69} resonance line, and obtain the result $\gamma = 2000$. Since the impurities used by Rhoderick were one electron donors or acceptors, we are reasonably confident that the effective charge at the impurity site is nearly $\pm$ e. Thus the effective strength of the quadrupole interaction is a factor of 2000 larger than predicted by this calculation for a point charge in a continuous dielectric medium.

We have made preliminary measurements on a GaAs sample that show qualitatively the same results as Rhoderick. In our case, however, we have induced vacancies in the sample by thermal damage - heating the sample to about 700°C, then rapidly quenching it to about room temperature. These vacancies then act as charge centers and create electric field gradients like impurities. We have observed both a decrease in NMR signal intensity and a change in NMR linewidth.

The decrease in signal is shown in Fig. 1 for the one sample observed so far. There is an orientation dependence of the signal intensity, which appears to be preserved even after the damage. Whether or not this is a real effect cannot be determined yet,since these numbers were obtained by measuring the peak-to-peak height of the derivative of the absorption curve, χ''. We use this number here because Rhoderick did, and we were interested in comparison with his data. However, this measurement does not accurately describe the changes in χ'' as impurities are introduced into the lattice, for if χ'' changes shape as well as intensity the single measurement of $\left.\frac{\partial \chi''}{\partial H}\right)_{max}$ might well lead to an incorrect interpretation of the number of nuclei contributing to the resonance.

We feel that it is incorrect to attribute the enhanced quadrupole effects caused by lattice defects - either impurities or vacancies - to the ordinary antishielding action of the electrons. In fact there is some indication that another process is involved, which is not totally understood, and which may not have been seen by Rhoderick. In Rhoderick's "pure" samples he found no line width change as a function of orientation in the magnetic field, and he explains this isotropic broadening using the pseudo-exchange interaction, in which the nuclei interact with each other through electrons.

R. K. Sundfors(6) has used NMR and nuclear acoustic resonance techniques to isolate broadening mechanisms in III-V compounds. Unlike Rhoderick he finds a dependence of the Ga^{69} second moment upon crystal orientation in the magnetic field. He attributes this to quadrupole broadening caused by a small random electric field gradient present in the lattice. We find the same angular dependence in an undoped specimen with 10^5 fewer charge carriers than Sundfors'. We feel that fewer charge carriers implies fewer substitutional impurities, which should cause much less broadening due to random electric field gradients. When damage is caused by thermal shock we find that the linewidth decreases in addition to the loss of intensity. These line width data are shown in Fig. 2. This behavior indicates that spin-spin relaxation is partially inhibited when the quadrupolar satellite shift occurs. Thus the sharp decrease in "intensity" (as defined by Rhoderick) may well not be entirely due to antishielding.

Some of these data were presented in an oral report at an American Physical Society meeting,(7) and the abstract for that report is included here as Appendix II.

The best way to monitor intensity is to integrate over the absorption curve χ'', but there is a difficulty in that a low signal to noise ratio in the extreme wings of the resonance causes very large experimental error. In order to make such measurements accurately, one must use signal averaging techniques. Much of the work of this past year has been devoted to purchasing and building the components of a system to do this. The system consists of an analog-to-digital converter, a small computer, and the interfacing required to make the various parts of the experiment work together. The signal averaging system is nearly complete, and is expected to be operating about June 1, 1972.

A pulsed NMR spectrometer has been completed and is now operating. This apparatus will assist in careful line shape and intensity measurements, and as well allow the application of the Waugh pulse techniques(4) to the problem.

III. CONCLUSIONS

Substantial progress has been made in preparation for the experimental and theoretical research on the main objective of this contract. The preliminary investigations have already found new and interesting results, some of which are being published. The sensitivity to thermally induced vacancies that we have found supports our hypothesis that we will be able to calibrate low concentrations of charged defects. A quantitative evaluation of the ultimate sensitivity of this technique must await more detailed studies of the NMR line shape and intensity. This phase of the experimental program will soon be aided considerably by the recently acquired signal averaging system.

It was hoped that the signal averaging system would be completed by the time of this report. The major component of that system is the small digital computer, for which an order was first place in late July, 1971. However, the order was held up by the Division of Automatic Data Processing under the Virginia Governor's office until November 18, 1971. This delay was purportedly to coordinate our purchase with state acquisition of other computers, although this federally-funded research project was not intended to be coordinated with other state computers or research projects. The outcome of this is a delay of approximately four months in beginning our full effort in taking data.

Some of the theoretical research done this past summer was carried out by A. Sher at the Aspen Summer Institute for Physics in Aspen, Colorado. This was done with the knowledge and consent of both the principal investigator and the technical officer of this contract.

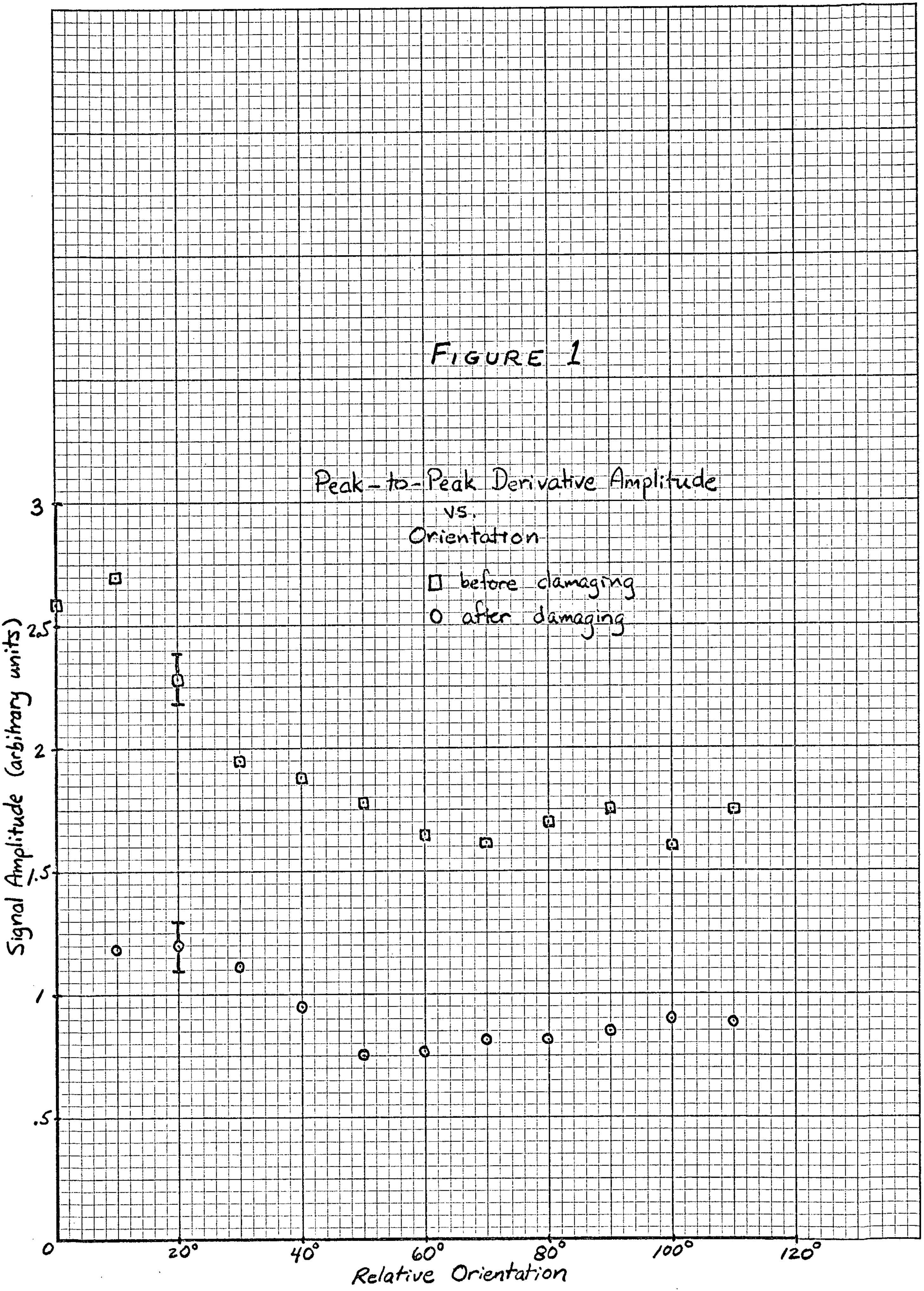


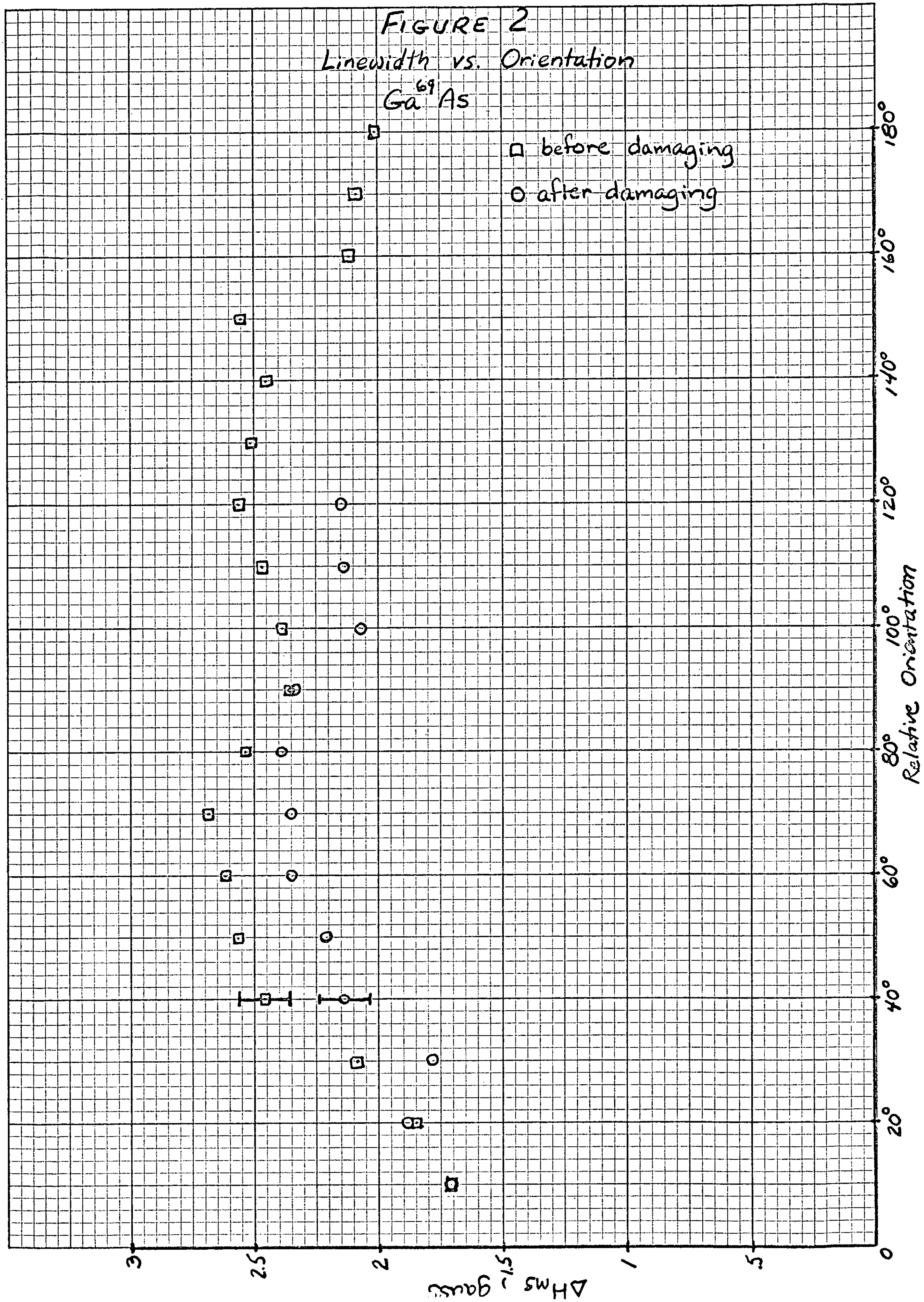
FIGURE 1

Peak-to-Peak Derivative Amplitude vs. Orientation

FIGURE 2

Linewidth vs. Orientation

$Ga^{69}As$



Appendix I

To gain some idea of the behavior of $\omega_{\vec{k}x}$, convert the sum over $\vec{\ell}$ to an integral from $\vec{\ell} = \vec{a}$ to $\ell = \infty$. If the upper limit on $\vec{\ell}$ is taken to be the size of the sample $\sim N^{1/3}$, then ω_{0x} is zero; if $\ell = \infty$ is used, then ω_{0x} is finite. Since this is a single point in k-space, it doesn't contribute much to integrals over $\vec{k}$ which will arise later in the theory; so practically no error is introduced. Also assume that the radial distribution function is uniform and equals $1/a^3$, i.e., this is a first approximation to a simple cubic lattice.

Denote a spherical harmonic by $Y_L^M(\Omega)$, where L is the angular momentum, M the z component of the angular momentum, and $\Omega = \theta, \varphi$. The second spherical harmonic $Y_2^0(\Omega)$ is

$$Y_2^0(\Omega) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1). \tag{A-1}$$

The function $e^{i\vec{k}\cdot\vec{\ell}}$ can be expanded in spherical harmonics as

$$e^{i\vec{k}\cdot\vec{\ell}} = 4\pi \left(\frac{\pi}{2k\ell}\right) \sum_{L,M} i^L Y_L^{M*}(\Omega)\, Y_L^M(\Omega_k)\, J_{L+1/2}(k\ell) \tag{A-2}$$

where $J_\nu(x)$ is a Bessel function of order ν with argument x. Using Eqs. (A-1) and (A-2), and converting the sum in Eq. (7) to an integral $\sum_{\vec{\ell}} \longrightarrow \int \frac{1}{a^3}\, d\vec{\ell} = \int \ell^2/a^3 \, d\ell \, d\Omega$, the expression for $\omega_{\vec{k}x}$ becomes

$$\omega_{\vec{k}x} \simeq \frac{\gamma^2\hbar}{4}\left(\frac{5}{16\pi}\right)^{-\frac{1}{2}} 4\pi \left(\frac{\pi}{2k}\right)^{\frac{1}{2}} \sum_{L,M} i^L Y_L^M(\Omega_k) \times \int_a^\infty \frac{d\ell\, \ell^2}{a^3 \ell^3 \ell^{1/2}} J_{L+1/2}(k\ell) \int d\Omega\, Y_L^{M*}(\Omega)\, Y_2^0(\Omega). \tag{A-3}$$

But the integral is

$$\int d\Omega\, Y_L^{M*}(\Omega)\, Y_2^0(\Omega) = \delta_{L,2}\,\delta_{M,0} \ ,$$

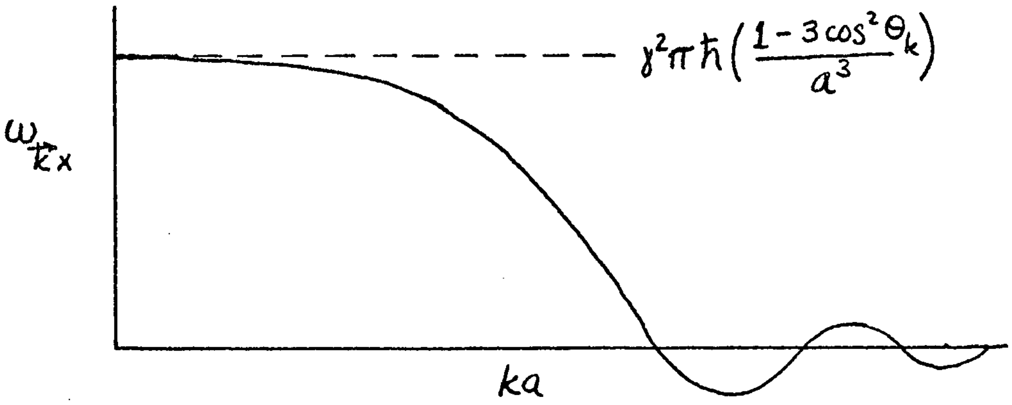
and when this is inserted into Eq. (A-3), it reduces to

$$\omega_{\vec{k}x} = \frac{\gamma^2\hbar}{4}\left(\frac{5}{16\pi}\right)^{1/2} 4\pi \left(\frac{\pi}{2k}\right)^{1/2} i^2\, \frac{Y_2^0(\Omega_k)}{a^3} \int_a^\infty dl\, \frac{J_{5/2}(kl)}{l^{3/2}} \ . \qquad \text{(A-4)}$$

The integral in Eq. (A-4) over l equals $k^{1/2} J_{3/2}(ka)/(ka)^{3/2}$ and $J_{3/2}(x) = \left(\frac{2}{\pi}\right)^{1/2}\left[\frac{\sin x}{x^{3/2}} - \frac{\cos x}{x^{1/2}}\right]$, so Eq. (A-4) can be simplified to

$$\omega_{\vec{k}x} = \gamma^2\hbar\pi\, \frac{(1-3\cos^2\theta_k)}{a^3}\left[\frac{\sin(ka)}{(ka)^3} - \frac{\cos(ka)}{(ka)^2}\right] . \qquad \text{(A-5)}$$

The frequency dispersion has the form



Appendix II

Abstract Submitted

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Physical Review
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Bulletin Subject Heading
in which Paper should be placed
Nuclear Magnetic Resonance

Antishielding Factor From Gallium Arsenide NMR.* R. HESTER, A. SHER, J. F. SOEST, College of William and Mary--Using the data of E. H. Rhoderick[1] on the intensity variation of the Ga^{69} NMR absorption derivative line with a change in the Te concentration of Te-doped GaAs, we calculate an effective antishielding factor on the order of 1000. This leads us to believe that the Ga^{69} resonance can be sensitive enough to detect defect concentrations in undoped GaAs possibly as small as 10^{14}-10^{15} cm^{-3}. Preliminary data taken by cw NMR have shown qualitatively the same results as Rhoderick has presented. The creation of defects by thermal damage, in the same manner as H. R. Potts and G. L. Pearson[2], lowers the intensity of the resonance line, and in addition, causes a line narrowing. This line narrowing may be the result of a partial quenching of one or more of the spin-spin interactions.

*Supported in part by NASA.

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