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Measurement of Electric Field Gradient Around Impurities in Certain Alloys of Aluminum[†]

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Using field-cycling double resonance, we have measured the quadrupolar couplings at different neighboring sites around seven impurities in aluminum. For the Ag, Mg, and Zn alloys, the field gradients at the nearest-neighbor sites are found to be greater than that at the next sites, while for the In, Ga, Ge, and Si alloys, the field gradients are greatest at the second-neighbor site and have a surprisingly high value. A study of the method is presented: In particular, we discuss the role of the cross-relaxation process between the quadrupole reservoir of the spins on the same shell around the impurity and the dipolar reservoir of the whole system.

I. INTRODUCTION

IN dilute alloys of aluminum the atoms surrounding the solute are not in a site of cubic symmetry. Consequently they are subjected to a nonvanishing electric-field gradient. Knowledge of the value of these field gradients in different shells around the impurity yields valuable information about the behavior of the conduction electrons. By measuring the variation of intensity of the NMR signal in high field as a function of the impurity concentration, in a large number of copper and aluminum alloys, various authors[1-4] have measured the number of neighboring nuclei subjected to field gradients greater than 6×10^{21} cm^{-3}. By the method of field cycling, Redfield[5] has obtained the value of these field gradients at the first and second neighbors in some copper alloys. We have continued these experiments using certain dilute alloys of aluminum.

After briefly recalling the principle of the experiment, we examine in Sec. II the irradiation process in zero field. In Sec. III, we describe the sample preparation. The results are presented in Sec. IV, and discussed in Sec. V.

II. THEORY

The principles of the experiment have already been described by Redfield. The spins are polarized in 3000 G at low temperature (1.4°K). The field is then cut off adiabatically. The spin system is irradiated in zero field with a rf field for a time τ (300 msec) of the order of T_1, the spin-lattice relaxation time (400 to 500 msec). The magnetic field is then switched on again and the fast passage signal recorded. This signal is proportional to $\beta_d=1/kT_d$, where T_d is the temperature of the dipolar reservoir at the end of the zero-field period.

In a simplified model, we can suppose that the alloy contains three kinds of nucleus. Nuclei A, far from impurities and defects, "see" field gradients which are smaller than the spin-spin interactions; it is the temperature of the dipolar reservoir of this ensemble which is measured. The nuclei B, situated near an impurity, can be separated into shells of equivalent sites subjected to the same field gradient. Lastly, we define a third species of nuclei, located near lattice defects (mainly dislocations) which, because of the basic structure of the defects, cannot be considered as distributed in shells of equal field gradient. One might think that when a photon is absorbed by a spin B in zero field, the energy is transmitted immediately to the ensemble of the spin system A by means of the strong spin-spin interaction. In fact, this is possible only when the photon-absorbing spin is near other spins subject to quadrupolar interactions sufficiently similar to permit energy transfer by the flip-flop mechanism[6]; if not, this cross-relaxation process cannot take place. On the other hand, the flip-flop transitions $\pm\frac{1}{2}$ always conserve energy in zero field. Hence, they permit a rapid spatial diffusion of energy, but it is only the dipolar energy of the B spins that is involved.

Consider the $n_q{}^B$ spins in one shell B, submitted to an electric-field gradient $V_{zz}=eq$ of axial symmetry, and irradiated by a rf field (ω, H_1). The Hamiltonian of interest for the quadrupole resonance of the B spins is

$$\mathcal{H}^B=\mathcal{H}_q{}^B+\mathcal{H}_d{}^B+\mathcal{H}_{\mathrm{rf}},$$

where $\mathcal{H}_q{}^B$ is the quadrupolar Hamiltonian restricted to the transition $\{\pm m\ \pm(m+1)\}$ at ω_q near ω, and $\mathcal{H}_d{}^B$ is the dipolar Hamiltonian of the B spins appropriately truncated.

Describing the B spins system by a density matrix

$$\rho_B=\frac{\exp(-\mathcal{H}_q{}^B\beta_q{}^B-\mathcal{H}_d{}^B\beta_d{}^B)}{\mathrm{Tr}[\exp(-\mathcal{H}_q{}^B\beta_q{}^B-\mathcal{H}_d{}^B\beta_d{}^B)]},$$

the evolution of the mean value of $\mathcal{H}_d{}^B$ and $\mathcal{H}_q{}^B$ is

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

[2] T. J. Rowland, Acta Met. **3**, 74 (1955).

[3] T. J. Rowland, Phys. Rev. **119**, 900 (1960).

[4] J. M. Brettel and J. Heeger, Phys. Rev. **153**, 319 (1967).

[5] A. G. Redfield, Phys. Rev. **130**, 589 (1963).

[6] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958); P. Pershan, *ibid.* **117**, 109 (1960).

given by[7,8]

$$\partial/\partial t\langle\mathcal{H}_d{}^B\rangle = -\Delta W_q(\Delta)C_B(\omega_q\beta_q{}^B - \Delta\beta_d{}^B)\,,$$
$$\partial/\partial t\langle\mathcal{H}_q{}^B\rangle = \omega_q W_q(\Delta)C_B(\omega_q\beta_q{}^B - \Delta\beta_d{}^B)\,,$$

where

$$\beta = 1/kT\,,\quad \Delta = \omega_q - \omega\,,\quad \omega_q = (2m+1)3e^2qQ/4S(2S-1)\,,$$
$$C_B = n_q{}^B[S(S+1) - m(m+1)]/k\,\mathrm{Tr}\rho_B\,,$$
$$W_q(\Delta) = \pi\gamma^2 H_1{}^2 g_q(\Delta)\,;$$

$g_q(\Delta)$ is the line shape of the quadrupole transition, $T_q{}^B$ and $T_d{}^B$ are the dipolar and quadrupolar temperatures of the B spin system.

Slusher and Hahn[9] have studied the diffusion of the dipolar energy for a very dilute system; in our case, the concentrations of the alloys are of the order of 10^{-3}, and we can suppose that the flip-flop transitions $\pm\frac{1}{2}$ give rise to a sufficiently rapid diffusion of the energy to define a single temperature T_d for the whole dipolar system. This hypothesis is confirmed by the experiments.

Thus, the first equation becomes

$$\partial/\partial t\langle\mathcal{H}_d{}^B\rangle = \partial/\partial t\langle\mathcal{H}_d\rangle = -\Delta W_q(\Delta)C_B(\omega_q\beta_q{}^B - \Delta\beta_d)\,,$$

where $\langle\mathcal{H}_d\rangle$ is the dipolar energy of all the spins.

We also have

$$\partial/\partial t\langle\mathcal{H}_d\rangle = -C_D\partial/\partial t\beta_d\,,\quad \partial/\partial t\langle\mathcal{H}_q{}^B\rangle = -C_Q\partial/\partial t\beta_q{}^B\,,$$

with

$$C_D = A^{-1}\,\mathrm{tr}\{\mathcal{H}_d{}^2\}\,,\quad C_Q = A^{-1}\,\mathrm{tr}\{(\mathcal{H}_q{}^B)^2\}\,,$$

A being proportional to the number of degrees of freedom of the whole system.

As mentioned above, it is necessary also to take account of cross relaxation between the quadrupolar and the dipolar systems. It is not simple to describe mathematically this cross relaxation, the experimental evidence suggesting that the transfer process is probably indirect, proceeding by way of spins around the dislocations.

Using a simplified model, one may write

$$\partial/\partial t\langle\mathcal{H}_q{}^B\rangle = -n_q{}^B\omega_q{}^2R_{DQ}(\omega)g_q{}'(\Delta)(\beta_q{}^B - \beta_d)$$
$$= -\partial/\partial t\langle\mathcal{H}_d\rangle\,,$$

where $R_{DQ}(\omega)$ is the cross-relaxation transition probability of a spin for a process in which energy ω_q is transferred to the dipolar reservoir; $g_q{}'(\Delta)$ is a cross-relaxation function related to the quadrupolar line shape.

Lastly, even in the absence of impurities and of lattice defects, there exists an absorption due to the dipolar bath[10];

$$\partial/\partial t\beta_d = -W_D(\omega)\beta_d\,,$$

with

$$W_D(\omega) = \pi\gamma^2 H_1{}^2 g_D(\omega)\omega^2\,,$$

$g_D(\omega)$ is the low-field line-shape function.

We are thus led to the equations

$$\begin{aligned}(\partial/\partial t)\beta_d &= -W_D(\omega)\beta_d + (1/C_D)\Delta W_q(\Delta)C_B(\omega_q\beta_q{}^B - \Delta\beta_d)\\ &\quad + (1/C_D)n_q{}^B\omega_q{}^2R_{DQ}(\omega)g_q{}'(\Delta)(\beta_q{}^B - \beta_d)\\ &\quad - (\beta_d - \beta_L)/T_{1D}\,,\\ (\partial/\partial t)\beta_q{}^B &= -(1/C_Q)\omega_q W_q(\Delta)C_B(\omega_q\beta_q{}^B - \Delta\beta_d)\\ &\quad - (1/C_Q)n_q{}^B\omega_q{}^2R_{DQ}(\omega)g_q{}'(\Delta)(\beta_q{}^B - \beta_d)\\ &\quad - (\beta_q{}^B - \beta_L)/T_{1Q}\,,\end{aligned}\tag{1}$$

T_{1D} and T_{1Q} are the spin-lattice relaxation times of the dipolar and quadrupolar reservoirs.

We consider several regions of applicability:

(A) The quadrupolar transition is at such a high frequency that the cross relaxation is negligible.

We have also, in this case, $W_D(\omega)\simeq 0$; and

$$\begin{aligned}(\partial/\partial t)\beta_d &= (1/C_D)\Delta W_q(\Delta)C_B(\omega_q\beta_q{}^B - \Delta\beta_d)\\ &\quad - (\beta_d - \beta_L)/T_{1D}\,,\\ (\partial/\partial t)\beta_q{}^B &= -(1/C_Q)\omega_q W(\Delta)C_B(\omega_q\beta_q{}^B - \Delta\beta_d)\\ &\quad - (\beta_q{}^B - \beta_L)/T_{1Q}\,.\end{aligned}\tag{1$'$}$$

A photon of frequency ω will yield energy ω_q to the quadrupolar and $-\Delta$ to the dipolar bath. Since the specific heat C_Q of the quadrupolar system is so small, $\beta_q{}^B$ will evolve quickly towards its equilibrium value $\omega_q\beta_q{}^{\mathrm{eq}} = \Delta\beta_d{}^{\mathrm{eq}}$. Meanwhile, since C_D is large and Δ small, β_d will change only by a small amount. So, the energy transferred to the dipolar reservoir will be very small and the fast passage signal will be nearly the same as without irradiation in zero field.

If we apply two rf fields such that $H_1 = H_2$ and $\Delta_1 = -\Delta_2$, i.e., symmetrically with respect to the center of the quadrupolar resonance,[11] Eq. (1′) gives

$$\begin{aligned}(\partial/\partial t)\beta_d &= -[2(C_B/C_D)\Delta^2 W_q(\Delta)]\beta_d\\ &\quad - (\beta_d - \beta_L)/T_{1D}\,.\end{aligned}\tag{2}$$

In this case, it is evidently possible to saturate completely the dipolar reservoir, with a time constant

$$T' = [2(C_B/C_D)\Delta^2 W_q(\Delta)]^{-1}.$$

(B) Cross relaxation occurs, the quadrupolar lines being at sufficiently low frequency.

We consider the case where the rf is centered on the line (i.e., $\Delta = 0$) and assume that the spin-lattice re-

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[7] M. Goldman and A. Landesman, Phys. Rev. **132**, 610 (1963).

[8] J. Levin, thesis, Grenoble, 1968 (unpublished).

[9] R. E. Slusher and E. L. Hahn, Phys. Rev. **166**, 332 (1968).

[10] A. G. Anderson, Phys. Rev. **115**, 863 (1959).

[11] J. Levin, M. Minier, D. Tunstall, and P. Averbuch, in *Proceedings of the Fourteenth Colloque Ampere*, edited by R. Blinc (North-Holland Publishing Co., Amsterdam, 1967), p. 114.

laxation $1/T_{1Q}$ is negligible compared with the cross relaxation.

A quasistationary value for $\beta_q{}^B$ results:

$$\beta_q{}^{\mathrm{qs}}=\beta_d\frac{n_q{}^B R_{DQ}(\omega)g_q{}'(0)}{C_B W_q(0)+n_q{}^B R_{DQ}g_q{}'(0)}=\beta_d\frac{1}{1+KH_1{}^2}.$$

Thus,

$$\frac{\partial}{\partial t}\beta_d=\left[-W_D(\omega)-\frac{1}{C_D}n_q{}^B\omega_q{}^2R_{DQ}g_q{}'(0)\frac{KH_1{}^2}{1+KH_1{}^2}\right]\beta_d$$
$$-\frac{\beta_d-\beta_L}{T_{1D}}. \quad (3)$$

This last equation is valid only on the assumption of a fast cross relaxation permitting $\beta_q{}^{\mathrm{qs}}$ to be attained in a time short compared with the irradiation time in zero field. It is to be noted that that part of the saturation time constant arising from the cross relaxation varies not as $H_1{}^2$, but rather as $KH_1{}^2/(1+KH_1{}^2)$.

When the rf is not centered on the line, the equations are not simple and the second term of Eq. (1) is no longer negligible: in fact, since the value of $\beta_q{}^{\mathrm{qs}}$ is mainly determined by the cross relaxation, the heat flow by dipolar energy diffusion does not cease as in the case of paragraph (A). Consequently, the experimentally observed line shape does not correspond in a simple way to the quadrupolar line shape.

The only way to obtain the line-shape function $g_q(\Delta)$ is by means of Eq. (2), making the assumption that the energy can diffuse sufficiently rapidly by the flip-flop mechanism to establish a dipolar temperature for the whole reservoir. This is possible only when the cross relaxation is negligible.

III. SAMPLE PREPARATION

The 0.5 and 0.05 at.% alloys of *Al*-Mg were supplied by the Pechiney Co. The powder, obtained by filing, was sieved and passed through the gap of a magnet to remove magnetic particles. Analysis by electron microprobe at this point indicated a good degree of homogeneity in the distribution of Mg in the interior of the particles. To remove the defects produced by filing, we were forced to anneal the samples. Many different thermal treatments were tried in argon, or in vacuum: 250 h at 200°C; 24 h and 2h at 500°C. These annealings were followed either by gradual cooling or by quenching in water. In every case the Mg content was found to diminish,[12] and furthermore its distribution became very inhomogeneous (Fig. 1). The change of concentration does not, of course, interfere with the measurement of the value of the field gradients on the first two or three shells, but it made impossible any study of concentration dependent effects.

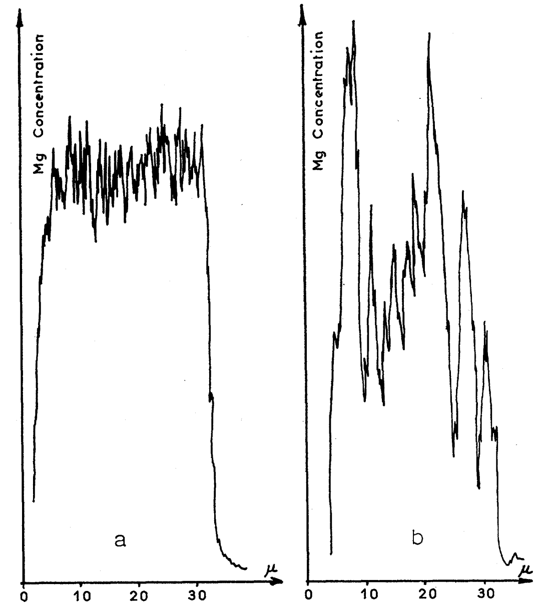

FIG. 1. Electron microprobe analysis of a powder of Al 0.5 at.% Mg: (a) before annealing; (b) after annealing for 2 h at 500°C.

The *Al*-Zn samples were prepared by dilution of an alloy containing 8 at.% Zn. Two kinds of annealing were carried out on the powder (2 h at 500°C and 24 h at 200°C), which gave analogous results.

For the other samples, aluminum of 99.999% purity was melted with the desired metal for a period of 4 h at 800°C. The temperature was lowered to 500°C, then the ingot was quenched in water. In the case of *Al*-Ge and *Al*-Ga, our results were essentially the same in powders annealed at 200 and 500°C. On the other hand, silver and indium, being very insoluble in aluminum, precipitate out on quenching the ingot and the resulting quadrupolar lines we observe are of low intensity. The powder was then kept for 24 h at 550°C, then quenched in water, thus considerably increasing the concentration of dissolved impurity atoms.

IV. EXPERIMENTAL RESULTS

In the experiments $k\beta_d(0)=150\ {}^\circ\mathrm{K}^{-1}$, $k\beta_D(\tau)$ being always $>10\ {}^\circ\mathrm{K}^{-1}$, and $k\beta_L=0.7\ {}^\circ\mathrm{K}^{-1}$. In Eqs. (2) and (3) it is therefore possible to put $\beta_L=0$, thus giving on integration

$$\beta_d(\tau)=\beta_d{}^{\mathrm{off}}(\tau)\exp[-2(C_B/C_D)\Delta^2W_q(\Delta)]\tau, \quad (4)$$

in the case where cross-relaxation is negligible, and

$$\beta_d(\tau)=\beta_d{}^{\mathrm{off}}(\tau)\exp-\left[W_D(\omega)\right.$$
$$\left.+\frac{1}{C_D}n_q{}^B\omega_q{}^2R_{DQ}g_q{}'(0)\frac{KH_1{}^2}{1+KH_1{}^2}\right]\tau, \quad (5)$$

when cross relaxation is the dominant process.

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[12] K. Forsvoll and D. Foss, Phil. Mag. 13, 329 (1966).

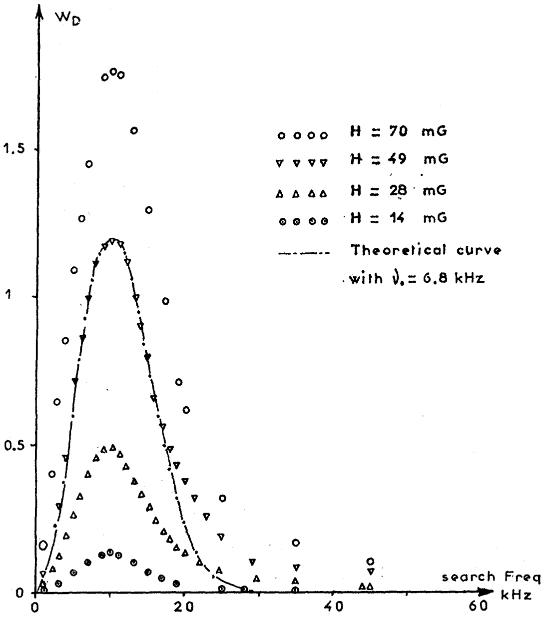

FIG. 2. Single-frequency irradiation in pure aluminum. Variation of $W_D(\omega)=\ln[(S^{\text{off}}-S_{\text{rec}})/(S-S_{\text{rec}})]$ with search frequency $\omega/2\pi$.

$\beta_d{}^{\text{off}}(\tau)$ is the final dipolar temperature in zero field with no irradiation.

Even starting out with an infinite dipolar temperature $1/k\beta_d(\tau)$, a signal is seen S_{rec} due to the partial recovery of the magnetization during the restitution of the field. It can be shown[13] that, in fact, this signal is independent of the starting temperature. Thus we have

$$S-S_{\text{rec}}\propto\beta_d(\tau).$$

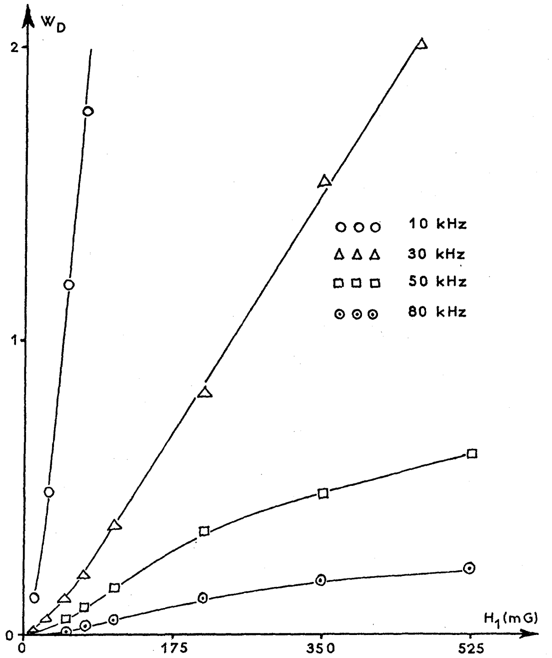

FIG. 3. Variation of $W_D(\omega)=\ln[(S^{\text{off}}-S_{\text{rec}})/(S-S_{\text{rec}})]$ with the amplitude of the rf field at different frequencies in pure aluminum.

Results on Pure Aluminum

The results are shown in Fig. 2. Also plotted is the theoretical absorption curve assuming a gaussian line shape:

$$g_D(\nu)\propto\exp(-\nu^2/2\nu_0{}^2).$$

The center of the line is in reasonable agreement with the theoretical form, taking $\nu_0=6.8$ kHz, but at higher frequencies the observed absorption is greater than that calculated on this model.

In Fig. 3, we plot the variation of $W_D=\ln[(S^{\text{off}}-S_{\text{rec}})/(S-S_{\text{rec}})]$ as a function of H_1, the amplitude of the rf field. It can be seen that at all frequencies no agreement exists between the foreseen $H_1{}^2$ dependence and that which is observed, except at very low values of $H_1(=40\text{–}50$ mG). It was further noticed that in the less pure samples not only was it necessary to use a larger value of ν_0 to fit the experimental curve, but also at higher frequencies the absorption is still too great. These observations would suggest that this continuous absorption background is due to the spins situated near the defects in the sample; the dislocations especially are trapped by the impurities, and their number increases with impurity content of the sample. Since the structure of these defects is not uniquely defined, the field gradients produced at the neighboring atoms form a continuous distribution, corresponding to a continuous absorption background.

The value of $\nu_0=6.8$ kHz, which agrees fairly well with the experiments, leads to a value of the Van Vleck second moment $\langle\Delta\nu^2\rangle=13.5$ kHz^2, which is considerably greater than the theoretical value of 9.29 kHz^2. This has already been observed by various workers, and appears to be due to residual quadrupolar interactions.

Results on *Al*-Mg

Four lines are observed, at 50, 100, 155, and 295 kHz, superimposed on the absorption background already observed in pure aluminum (Fig. 4). The background absorption, extremely large in the unannealed samples, is markedly reduced by thermal treatment, but remains more visible in the case of the more concentrated samples.

It is probable that many dislocations remain trapped by the impurities. In an unannealed sample of 0.05 at.% the cross relaxation permits our observation of the lines at 50, 100, and 155 kHz with a single frequency at zero field. After annealing it becomes necessary to use the double frequency technique to observe the line at 155 kHz.[14] The 295-kHz line behaves in the same

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[13] M. Minier, thesis, Grenoble, 1968 (unpublished).

[14] M. Minier, Phys. Letters **26A**, 548 (1968).

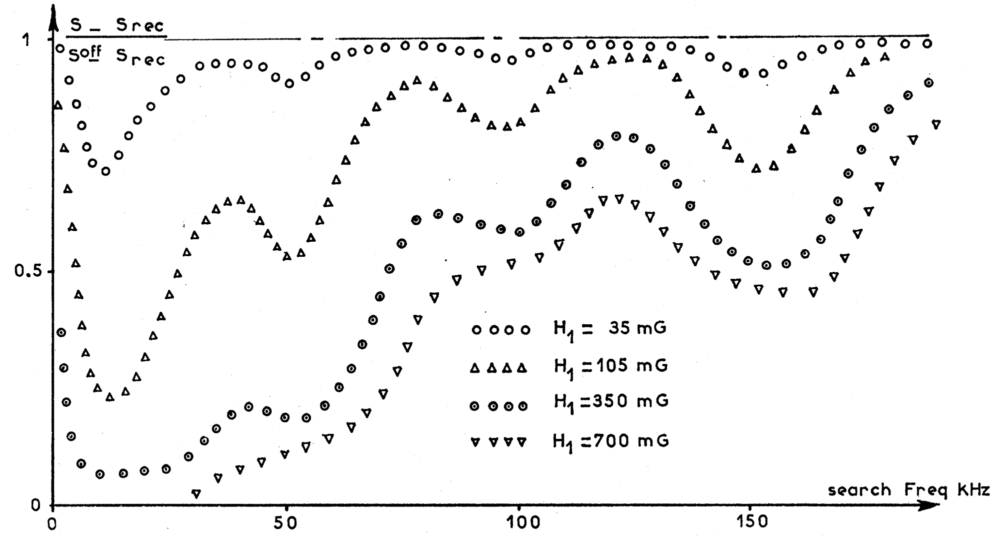

FIG. 4 Single-frequency irradiation in Al 0.4 at.% Mg.

way in a sample of 0.5 at.% Mg. This fact illustrates the role of the dislocations in the energy-transfer process: Either they greatly broaden the lines, giving rise to overlapping of the wings and consequent easing of the cross-relaxation process, or else, which seems to us to be the more likely, the transfer proceeds with the help of the spins near the dislocations. A spin in an irradiated shell transfers its quadrupolar energy to another spin which, close to a fault, is subjected to a similar field gradient. If, as the continuous absorption background would seem to show, the field gradients around a defect form a continuum the energy transfer to the dipolar bath is facilitated.

We have attempted to verify the theory of Sec. II on the resonance lines at 50, 100, and 155 kHz when cross-relaxation time is sufficiently short.

One can plot the curves of $\ln[(S^{\text{off}}-S_{\text{rec}})/(S-S_{\text{rec}})]$ as a function of H_1 at 50, 100, and 155 100, and 155 kHz.

This gives quantities which ought to have the form

$$W_D'(\omega)+(1/C_D)n_q{}^B\omega_q{}^2R_{DQ}g_q'(0)\times[KH_1{}^2/(1+KH_1{}^2)], \quad (6)$$

where $W_D'(\omega)$ represents the absorption by spins other than on the shell under consideration; $W_D'(\omega)$ is estimated by interpolation using these same curves far away from the resonances, that is to say at 75, 125, and at 175 kHz. Thus, in Fig. 5 we plot the variation of the second term of formula (6). The curves at 100 and 155 kHz agree excellently with a dependence of the form $KH_1{}^2/(1+KH_1{}^2)$, particularly if one recalls that the model which we have used is extremely crude. For the 50-kHz line, the accuracy is considerably lower, since the value of $W_D'(\omega)$ is very uncertain but its behavior is similar.

Since we do not know either $R_{DQ}(\omega)$ or $g_q'(0)$ for the various lines, it is difficult to extract more information, and in particular it is impossible to deduce the value of $n_q{}^B$ for each shell.

Lastly, an examination of the 295-kHz line with the double-frequency technique gives results similar to those obtained on *Al*-Ag, *Al*-Ge, and *Al*-Si which are discussed later.

Results on *Al*-Zn

Using single-frequency irradiation in zero field, we observe the resonances at 27 and 55 kHz already seen by Fernelius.[15] Because the cross-relaxation time is

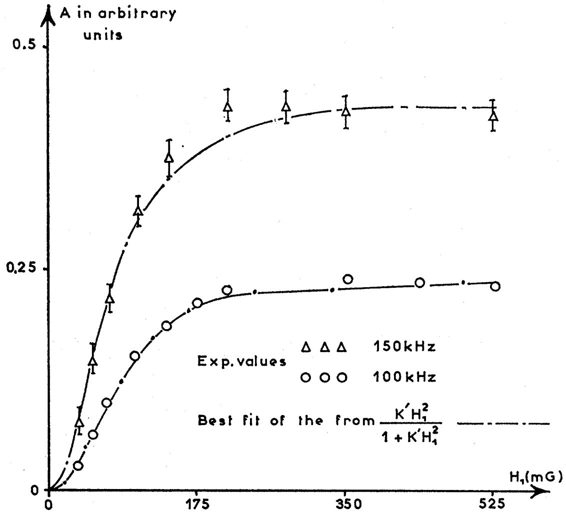

FIG. 5. Study of the cross-relaxation term $A=(1/C_D)n_q{}^B\omega_q{}^2R_{DQ}(\omega)g_q'(0)(KH_1{}^2/1+KH_1{}^2)$ in Al-Mg.

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[15] N. Fernelius, in Ref. 11, p. 497.

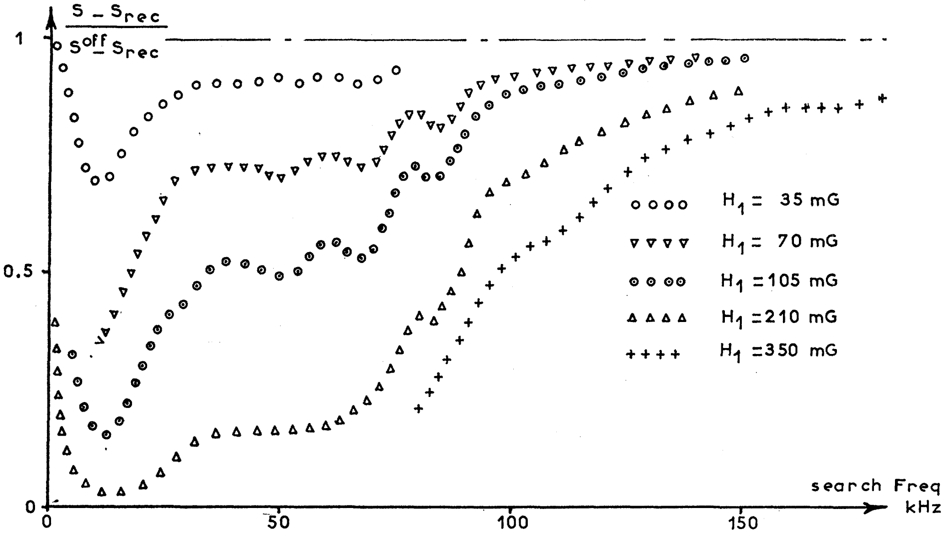

FIG. 6 Single-frequency irradiation in Al 0.1 at.% Ag.

shorter on account of the greater number of defects in our samples, we are also able to resolve a line at 158 kHz. Use of the double-frequency technique shows another line at 275 kHz.

The results obtained from all the samples are summarized in Table I. In *Al*-Ag the position of the line near 40 kHz is uncertain (see Fig. 6). In *Al*-Si the resonance at 125 kHz is doubtful, and in *Al*-Ge there are at least two lines between 25 and 50 kHz (Fig. 7).

In the case of *Al*-Ge, the line at 252 kHz is intense and easy to study (Fig. 8). The intensity varies as H_1^2 up to values of 1 G^2, showing that our assumption of rapid dipolar energy diffusion is justified in this case. The variation of $1/T'$ with the frequency separation 2Δ between the two search fields, and the line shape $g_q(\Delta)$ which may be inferred by application of Eq. (2) are plotted in Fig. 9. With our experimental error, it is not possible to evaluate $g_q(\Delta)$ for $\Delta < 1$ kHz, but we can place the upper limit to the linewidth at half-height at 4 G. This value is very much less than in pure aluminum, but it is not too surprising considering that the truncation of the dipolar Hamiltonian of the spins in a shell near an impurity will be fairly drastic. We have already obtained a comparable result for *Al*-Ag,[16] but the accuracy of the measurement was considerably lower.

V. ANALYSIS AND DISCUSSION OF RESULTS

The first problem is the assignment of the observed lines to the different shells around the impurity; for

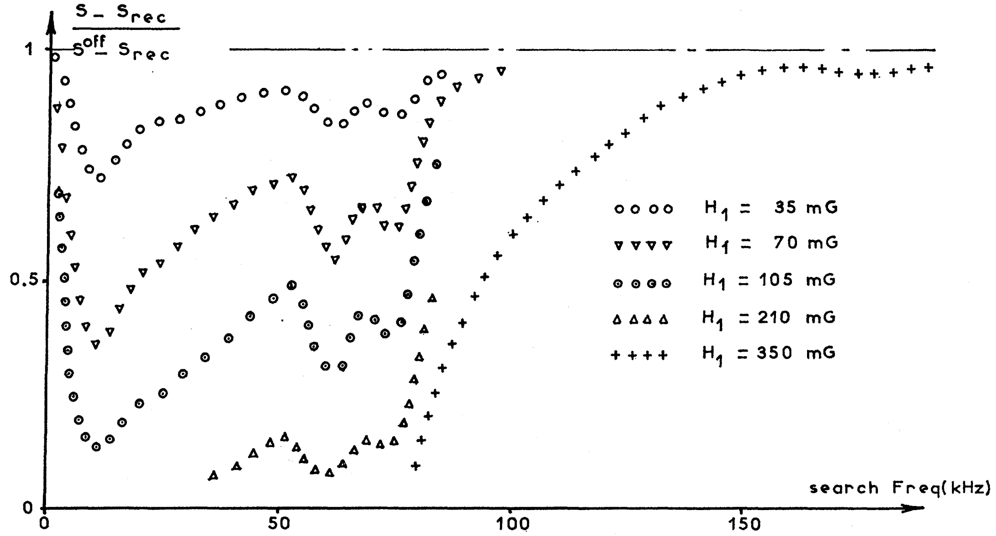

FIG. 7 Single-frequency irradiation in Al 0.2 at.% Ge.

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[16] M. Minier and Cl. Berthier, in *Proceedings of the Fifteenth Colloque Ampere* (to be published).

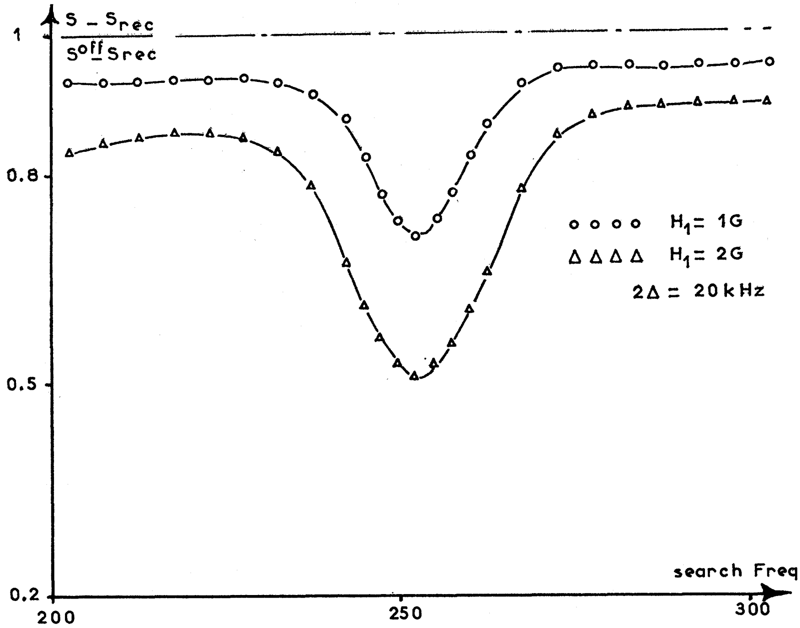

FIG. 8. Double-frequency irradiation in Al 0.2 at.% Ge.

this purpose, we have the following considerations to take into account:

(i). In Al, which has spin $\frac{5}{2}$, one should observe two quadrupolar transition frequencies $\nu(\pm\frac{1}{2}, \pm\frac{3}{2})$ and $\nu(\pm\frac{3}{2}, \pm\frac{5}{2})$, where $\nu(\pm\frac{3}{2}, \pm\frac{5}{2}) \leqslant 2\nu(\pm\frac{1}{2}, \pm\frac{3}{2})$, the equality sign relating to sites of axial symmetry. Among the near neighbors which we are able to see, only the sites on the second have uniaxial symmetry.

(ii). The number of nuclei on the different shells centered on the impurity are 12, 6, 24, 12,···, so we might expect to identify the lines by their intensities. Unfortunately, this is not conclusive evidence in our experiments. In fact, if one observes the line with a single frequency, using formula (6), one may, in favorable cases where the lines are well resolved, compare the values of $n_q{}^B\omega_q{}^2R_{DQ}(\omega)g_q{}'(0)$ for each line. But, since we know neither $R_{DQ}(\omega)$ nor $g_q{}'(0)$, it is not possible to go further.

(iii). The value of the field gradients should *on average* decrease with increasing distance from the impurity, but the oscillations permit inversions between neighboring shells.

TABLE I. Pure quadrupolar resonance frequencies in certain aluminum alloys.

	Z	Lines seen by single-frequency irradiation in zero field (in kHz)				Lines seen by double frequency irradiation (in kHz)	
Ag	−2	40[a]	50	67	83	190	330
Mg	−1	50	100	155		295	
Zn	−1	27	55	158		273	
Ga	0	25[a]	45			175	350
In	0	52	85			270	
Si	+1	45	86	125 (?)		217	434
Ge	+1	30	40	62	74	252	505

[a] Position uncertain.

(iv). Lastly, we have made a search for quadrupolar lines up to 1.7 MHz. The experiments of Rowland[2] and Brettel and Heeger[4] show that the existence of lines above 1.7 MHz is practically excluded.

Thus, in *Al*-Zn we may assign the transitions at 158 and 273 kHz to the first neighbors and the 27–55 kHz transitions to the second neighbors. These results

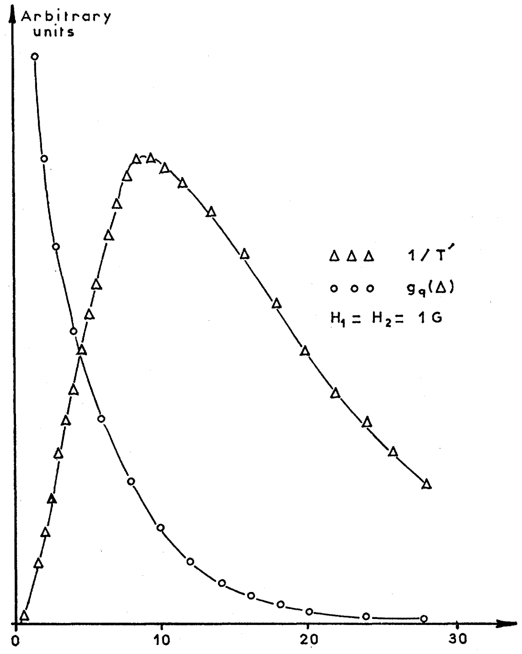

FIG. 9. Study of the line at 252 kHz in Al 0.2 at.% Ge.

TABLE II. Experimental values of the electric field gradient at the first two shells around the solute atoms.

	Shell 1 $q(10^{21}\ \mathrm{cm}^{-3})$	η^{a}	Shell 2 $q(10^{21}\ \mathrm{cm}^{-3})$	Charge difference Z	Lattice strain parameter[b] $1/a\ da/dc$	Effective charge difference[c] Z_{eff}
Ag	215	0.34 ± 0.04	52[d]	-2	0	-2
Mg	185	0.12 ± 0.06	63	-1	0.097	-1.6
Zn	180	0.35 ± 0.03	35	-1	-0.016	-0.90
Ga	<35		220	0	0.044	-0.26
In	<65		340[d]	0	0	0
Ge	<55		320	1	0.044	0.74
Si	<75		275	1	-0.037	1.22

[a] Asymmetry parameter using the M. H. Cohen tables, Ref. 19. [b] See Ref. 20. [c] See Ref. 21. [d] Assignment uncertain.

are in agreement with those of Drain.[17] In *Al*-Mg the lines at 50 and 100 kHz for the second, and 155 and 295 kHz for the first neighbors have been confirmed by Fernelius.[18]

In *Al*-Ag we believe that the lines at 190 and 330 kHz can be due only to the two quadrupolar transitions of the first neighbors; the assignment of the other lines is less certain.[16]

In *Al*-Ga we can explain the lines at 350 and 175 kHz only by attributing them to the second neighbors, the nearest site to the impurity with axial symmetry. We interpret in the same way the lines at 217 and 434 kHz in *Al*-Si and 252 and 504 kHz in *Al*-Ge, although it is very surprising to find for all these samples the second neighbors are subjected to a field gradient which is greater than at the first neighbors and has such a high value.

The assignment of the other resonance lines is very difficult, and at the moment cannot be made on any firm basis.

In the case of *Al*-In we had difficulty in observing the line at 270 kHz; in fact, on account of the very poor solubility of this metal in aluminum there were certainly less than 500 ppm In atoms dissolved. No other line was observed between 135 and 540 kHz. In all the alloys studied, when the transitions were visible only by the double irradiation technique, it was always noted that the $\frac{1}{2}$–$\frac{3}{2}$ line was much more intense than the $\frac{3}{2}$–$\frac{5}{2}$ line. Thus, if the line at 270 kHz were a $\frac{3}{2}$–$\frac{5}{2}$ transition, it is probable that we would see a line about 135 kHz. If, on the other hand, it represents the $\frac{1}{2}$–$\frac{3}{2}$ transition, it is very likely that we would not be able to see the correspondings $\frac{3}{2}$–$\frac{5}{2}$ transition; if, moreover, we remember the similar behavior of Mg and Zn (charge difference with aluminum $Z=-1$) on the one hand, and of Ge and Si ($Z=+1$) on the other, and compare the results with gallium ($Z=0$), it seems probable that this line is due to the second nearest neighbors. The results are summarized in Table II.[19–21]

TABLE III. Values of δ_0, δ_1, α, and μ in the alloys *Al*-Zn and *Al*-Mg ($\Delta\rho$ in $\mu\Omega$ cm/at. %).

	Z_{eff}	$\Delta\rho$	δ_0	δ_1	α	Φ
Zn	-0.90	0.23	-0.5	-0.30	0.42	0
Mg	-1.60	0.46	-2.45	-0.03	0.64	-2.45

It would be desirable to compare these results with the values calculated from the approach of Blandin and Friedel[22] or Kohn and Vosko[23]; since the method is an asymptotic one, only very crude agreement is expected for the first neighbors. For *Al*-Mg and *Al*-Zn we have recalculated the various parameters already evaluated by Blandin and Friedel (Table III), since the currently accepted values of the residual resistivities[24,25] are different from those used by these authors.

We denote by Z_{eff} the effective charge difference between the matrix and the impurity, by $\Delta\rho$ the residual resistivity (in $\mu\Omega$/at.%), by δ_0 and δ_1 the phase shifts of the *s*- and *p*- wave functions, and by q the field gradient.

We have

$$q(r)=\frac{4}{3\pi}\mu\alpha\frac{\cos(2K_F r+\Phi)}{r^3},$$

where α and Φ are related to δ_0 and δ_1, and μ is a factor depending on the band structure at the Fermi level in the pure metal.

Using Rowland's measurements[2] of the wipe-out number, we have to take $\mu=12$. The field gradients thus obtained at the sites neighboring a Zn or Mg atom are shown in Table IV.

Comparison of the theoretical values of the electric-field gradient with the experimental measurement in Table II shows that it is impossible to reconcile the two results. Even with a different value of the coefficient μ, one cannot explain simultaneously the observed field gradient on the first and second neighbors. A correction taking into account the displacements of the atoms

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TABLE IV. Field gradients (in units of 10^{21} cm^{-3}) in *Al*-Zn and *Al*-Mg.

Shell	1	2	3	4	5	6	7
Zn	79	4.1	4.8	4.7	8.1	6.1	1.5
Mg	45	26	12	5	10	8.4	6.5

around the impurity, using an elastic model,[21] modifies only slightly the theoretical values. The improved resistivity values we have used do not, in fact, produce any better agreement with the experimental results.

In *Al*-Ag, *Al*-Si, and *Al*-Ge, the values of $\Delta\rho$ furnish several estimates of δ_0 and δ_1, but in each case the disagreement with the experimental results is complete.

It would be worthwhile to use a method with greater validity at the level of the first neighbors, for example by taking into account a preasymptotic term[26] in R^{-4}, or else by treating simultaneously the size and charge effects of the impurity as has been done by Beal-Monod and Kohn.[27]

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Microwave Spectroscopy of OH⁻ Ions in the KCl and NaCl Lattices*

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Microwave resonant absorption has been observed in OH$^-$-doped KCl and NaCl crystals. Several lines were observed from 8–40 GHz by using relatively standard microwave spectroscopic techniques. The zero-field spectra obtained here indicate that the OH$^-$ ion experiences a strong C_{4v} potential in addition to the expected octahedral crystal field. The C_{4v} potential probably arises from a shift of the OH$^-$ center of mass from the lattice site.

I. INTRODUCTION

ELECTRIC ordering and dielectric relaxation experiments[1,2] have indicated that the OH$^-$ ion is trapped sustitutionally in place of a Cl$^-$ ion in the KCl lattice and that the diatomic ion is aligned along one of the six ⟨100⟩ axes of the crystal. Apparently, the diatomic ion is best characterized as a tunneling librator[3,4] instead of a hindered rotor.[5,6] More recently, paraelectric resonance of the OH$^-$ ion in KCl has been observed at 35,[7] 24,[8] and 9 GHz.[9] The paraelectric resonance technique is a fixed-frequency experiment where a dc electric field is swept until a difference between tunneling states coincides with the fixed microwave frequency. By choosing an appropriate model, one can assign the paraelectric transition and then extrapolate back to the zero external field. Several zero-field models have been proposed[4,10,11] which account for the above paraelectric experiments and also the near- and far-infrared experiments[12–14] and the thermal

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