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NUCLEAR MAGNETIC RESONANCE IN AL-MN ALLOYS

by

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ABSTRACT

This thesis reports on the behaviour of the n.m.r. signal from Al^{27} in Al and Al Mn alloys. We have obtained values of 0.162 .002% for the Knight shift and of 8.65 .2 oe. for the line width in pure Al, in good agreement with values reported elsewhere.

On alloying with Mn, decreases in intensity, line width and Knight shift are observed. This behaviour is readily explained by nuclear electric quadrupole interactions.

The small effective magnetic moment of the Mn ions seems to have a negligible effect on the line and from that point of view Al Mn behaves essentially like Al Mg and Al Zn which have been extensively studied recently.

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CHAPTER I

INTRODUCTION

The non-magnatic behaviour of Al-Mn alloys has been studied recently through low temperature resistivity (Hedgcock et al, 1960) and magnetic susceptibility (Collings and Hedgcock, 1961) measurements. A nuclear magnetic resonance (n.m.r.) study of the same alloys was undertaken in order to obtain additional confirmation of this behaviour. The temperature independence of the line width, which we have observed, provides this confirmation.

Additional evidence has also been found to verify the influence of quadrupole effects on the n.m.r. line. Dislocations produced on filing the specimens are found to be particularly effective in causing large decreases in intensity, line width and Knight shift. We have been unable to determine the relative influences of dislocations and impurities, but the results indicate that the impurities "lock in" the dislocations and therefore are only indirectly involved.

We do not attempt to review the theory or to summarize the results obtained elsewhere. We report only the results obtained on Al-Mn alloys and attempt an explanation of these results. We refer to articles on n.m.r. by Andrew (1956), on the Knight shift by Knight (1956) and by Milford (1960) and on quadrupole effects in solids by Cohen and Reif (1957) for the basic theory of n.m.r.

CHAPTER II

EXPERIMENTAL

2.1 - Apparatus

The apparatus consisted of a marginal oscillator of the Pound-Knight type as modified by Teeters (1945). A d.c. signal, proportional to the derivative of the absorption curve, was recorded on an Esterline-Angus pen recorder. A complete description of the apparatus is available elsewhere (Frakman, 1960). The only modification was a replacement of the audio frequency phase and gain controls by a set described in Teeters' thesis. Interactions among the various units and between the controls of each caused some difficulty in the original system. A circuit diagram is included for completeness (Fig. 1).

The magnetic field of 6770 oe. was supplied by a large permanent magnet enclosed in a thermostatically controlled oven. To further improve the stability of the field, the controller itself was placed in the oven. In this way, the field can be kept constant to 0.1 oe. over a period of a day.

Frequency is swept slowly through resonance. By beating this slowly varying radio frequency against a standard frequency and observing the Lissajous figures obtained on an oscilloscope, it is possible to place frequency markers on the recorder chart. Although it is possible to calibrate the recorded signal to the nearest 10 c.p.s.,

nevertheless deviations between readings are such that measurement to the nearest 100 c.p.s. only is justified. The standard is checked periodically by testing it against WWV or CHU.

In order to extend the measurements to low temperatures, a cryostat has been constructed. An arrangement similar to that of Pascalillo (1956) has been used to mount the samples. Specimens are attached vertically in a lucite capsule attached to the end of a rod which extends, inside a glass tube, into the magnetic field. The specimen coil is wound around the lower end of the glass tube. In this way, several samples can be lowered from the top of the cryostat into position, in turn, an arrangement which is ideal both for flight shift measurements and measurements at low temperatures. The target assembly and specimen coil as well as dewars, vacuum valves and gauges are mounted on a carriage which allows precise positioning of the specimen in the magnet gap.

Several experiments have been performed at liquid nitrogen temperature as well as a single one at 4.2 K. The results obtained are not suitable for inclusion here, but from the success of this initial work it seems clear that no difficulties should be encountered in continuing measurements at low temperatures.

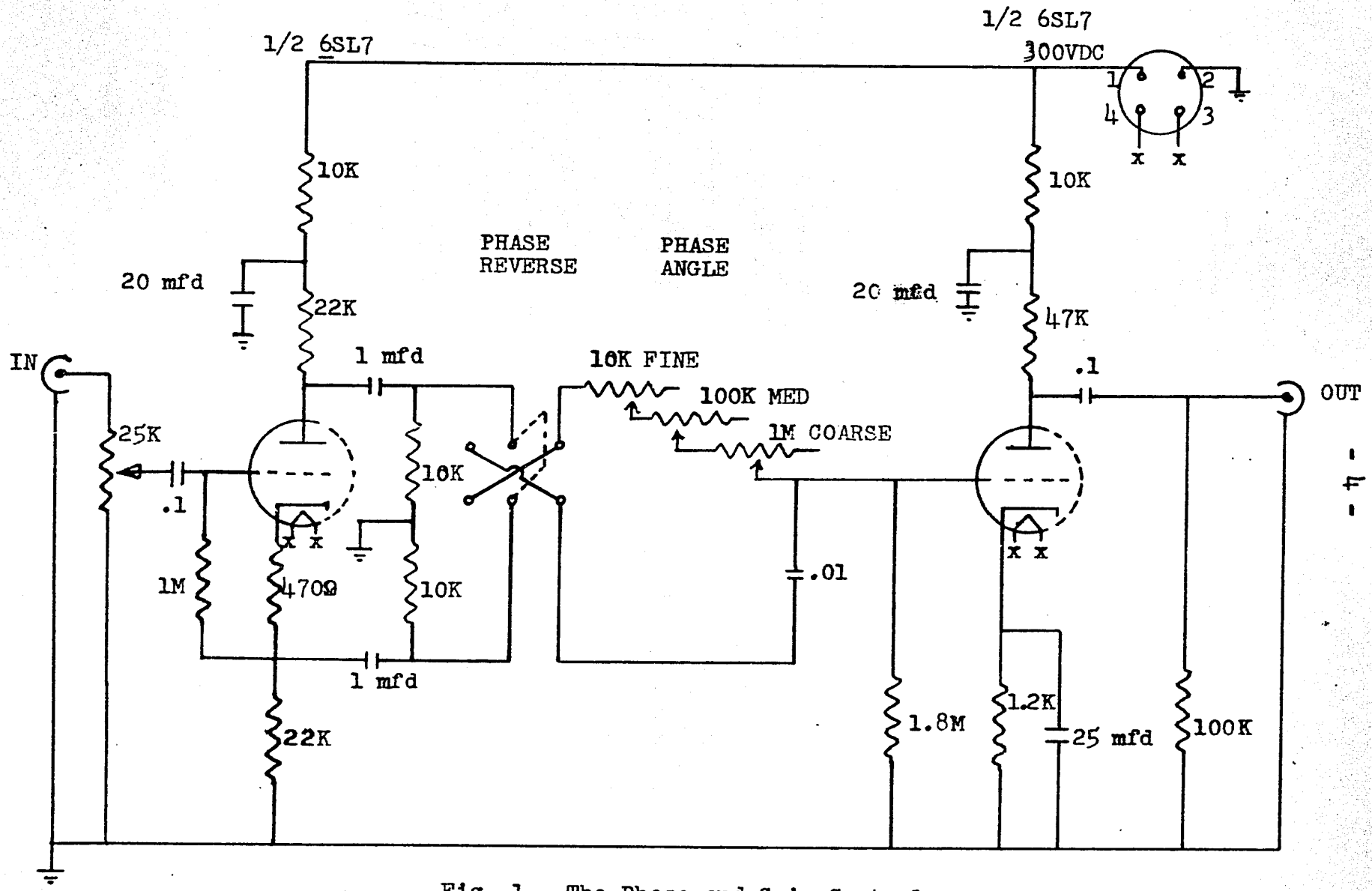

Fig. 1 - The Phase and Gain Control

2.2 - Sample preparation

Alloys are prepared by melting the proper quantities of Al and In in graphite crucibles which are sealed in quartz vials under 1/3 atm. of helium at room temperature. Both metals were of 99.99 purity, the Al being obtained from the Aluminum Co. of Canada, the In from Johnson-Mathey. During the melt, the vials are shaken periodically to ensure good mixing of components. The alloys are quenched from the melt in ice water. Afterwards, they are given a homogenizing anneal and quenched again. Powdered specimens are prepared by filing with a motor driven file. Only those filings which pass through a 325 mesh (43) sieve are retained. A good portion of the particles are smaller than this. The skin depth in pure Al is of the order of 30 . Skin depth effects, which could result in a distortion of the line or in a possible displacement of it, are therefore kept to a minimum. In any event, these would be effective only in the pure Al samples since, in the alloys, the skin depth is greater than the size of the particles. At low temperatures, skin depth effects become important in the alloys also. For ease of handling, the powders are cast in paraffin. Specimens 0.23"x 0.30" long are prepared.

2.3 - Measurement of field homogeneity:

It is important that the specimen coil remain in the same position in the field, in a region of maximum field homogeneity. The carriage on which the cryostat is mounted

allows the coil to be displaced in two directions. No displacement is allowed in the third direction in order to accommodate the dewars. The region of maximum homogeneity is located by observing the line width of Al^{27} in $AlCl_3$ solution as the position of the coil is varied. In the optimum region, the maximum field inhomogeneity is about 0.1 oe. as found when comparing the observed peak to peak line width of 0.2 oe. to the value of 0.07 oe. given by O'Reilly (1960). The coordinates of the position of the coil with respect to two reference axes enable the coil always to be placed in the same location within about 0.01 cm.

2.4 - Residual Resistance Measurements.

The n.m.r. signal is very sensitive to the presence of impurity atoms in the lattice (see below). The alloys were prepared in graphite to eliminate re actions between Tl and quartz and observed from the melt to ensure that the Tl remained in solid solution. Despite these precautions, it soon became evident that some means of determining the concentration of Tl in solid solution in Al was required. The usual methods of chemical or spectrographic analysis do not suffice.

It was suggested that residual resistance ratios defined as $\frac{R_{4.2}}{R_{300}}$, where $R_{4.2}$ is the resistance of the samples at 4.2 K and R_{300} their room temperature resistance, be used in determining concentrations. Some measurements on Al-Tl alloys (Feldgood et al, 1960) indicate that the resistance ratio is proportional to concentration

for low concentrations of Ni. These results were extrapolated to higher concentrations (Fig. 2). No measurements were made to determine residual resistance ratios for all samples. The values obtained were then used to find the concentration of Ni in Al.

2.3 - N.M.R. Measurements.

The spectrometer contains a calibrator by which it is possible to compare the signal intensities to known audio frequency voltages. This method was discarded since the calibration proved to be too sensitive to the settings of the various controls of the spectrometer. Intensities were finally measured by comparing the peak to peak amplitudes of the derivatives of the n.m.r. signal in the alloys to the amplitude in pure Al for each set of measurements. Care was taken to keep the gain of the circuit as well as the r.f. level constant during this time.

The line widths measured are the separation of the maxima and minima of the derivatives. This line width has been chosen in preference to the width at half maxima or to the r.m.s. line width (second moment) because of the ease with which it is observed. The second moment is useful when a comparison of experimental line widths and the theoretical widths, derived from Van Vleck's treatment of dipolar broadening, is desired. This thesis, however, is more concerned with the variations in width as alloying. Consequently, no attempt has been made to calculate second moments

nor to study line shapes.

Knight shifts of Al^{27} in Al and Al-Mn alloys are determined by comparison with a signal from $AlCl_3$. It is of interest to point out a correction which has to be introduced when the resonant frequency of a metallic specimen is measured. The noise bandwidth of the apparatus is dependent on the output RC time constant of the phase sensitive detector. For broad weak signals, a long time constant is required in order to obtain good signal to noise ratio. Time constants of 4 seconds and of 3 minutes have been used for $AlCl_3$ respectively. The effect of the long time constant is to shift the signal in time by an amount of the order of the time constant. This leads to an apparent increase in the value of the resonance frequencies. This increase is large for metallic specimens. To determine its value, the absolute value of the shift has been measured for the pure Al metal sample by using a much shorter time constant. Once it has been done, a correction may be applied to all measurements taken with the long time constant. Of course care must be taken to always sweep through the resonance from the same direction.

CHAPTER III

RESULTS

In Table I are shown the results of intensity, line width and Knight shift measurements in Al-Mn alloys vs. increasing concentration of Mn. They are shown graphically in Figs. 3, 4 and 5. These results are the mean values of a large number of measurements (25 or more), the errors quoted being r.m.s. deviations from the mean. Table I also lists the results of residual resistance measurements which were made on a portion of each alloy prepared (column (2)). Column (3) shows the concentrations of Mn in solid solution determined from these measurements and the extrapolated data of Wallingford which is shown in Fig. 2. The dangers inherent in making the extrapolation are fully realized. Our only justification is that the nominal values of concentration (column (4)) and those determined from residual resistance ratios sometimes agree. Where agreement indicates that the Mn has remained in solution, the nominal values of concentration are assumed correct. Where serious discrepancies occur, the values obtained from residual resistance measurements are used.

The value of 0.162±.002% reported here (5) for the Knight shift in pure Al agrees well with values of 0.162%

TABLE I. Measurements

(1) Specimen Number	(2) Resistance Ratio	(3) Mn Conc. percent	(4) Mn Conc. (nom.) percent	(5) Knight shift percent	(6) Line width oe.	(7) Relative Intensity
13		0	0	0.162 .002	8.65 .2	1
17	0.35	0.12	0.15	0.162 .002	8.6 .2	0.74 .04
15	0.70	0.28	0.25	0.160 .002	8.0 .2	0.48 .03
9	1.15	0.41	1.0	0.157 .002	7.6 .2	0.44 .04
8	1.24	0.48	0.5	0.156 .002	7.5 .2	0.36 .02
10	1.67	0.60	0.7	0.150 .002	7.4 .2	0.35 .02

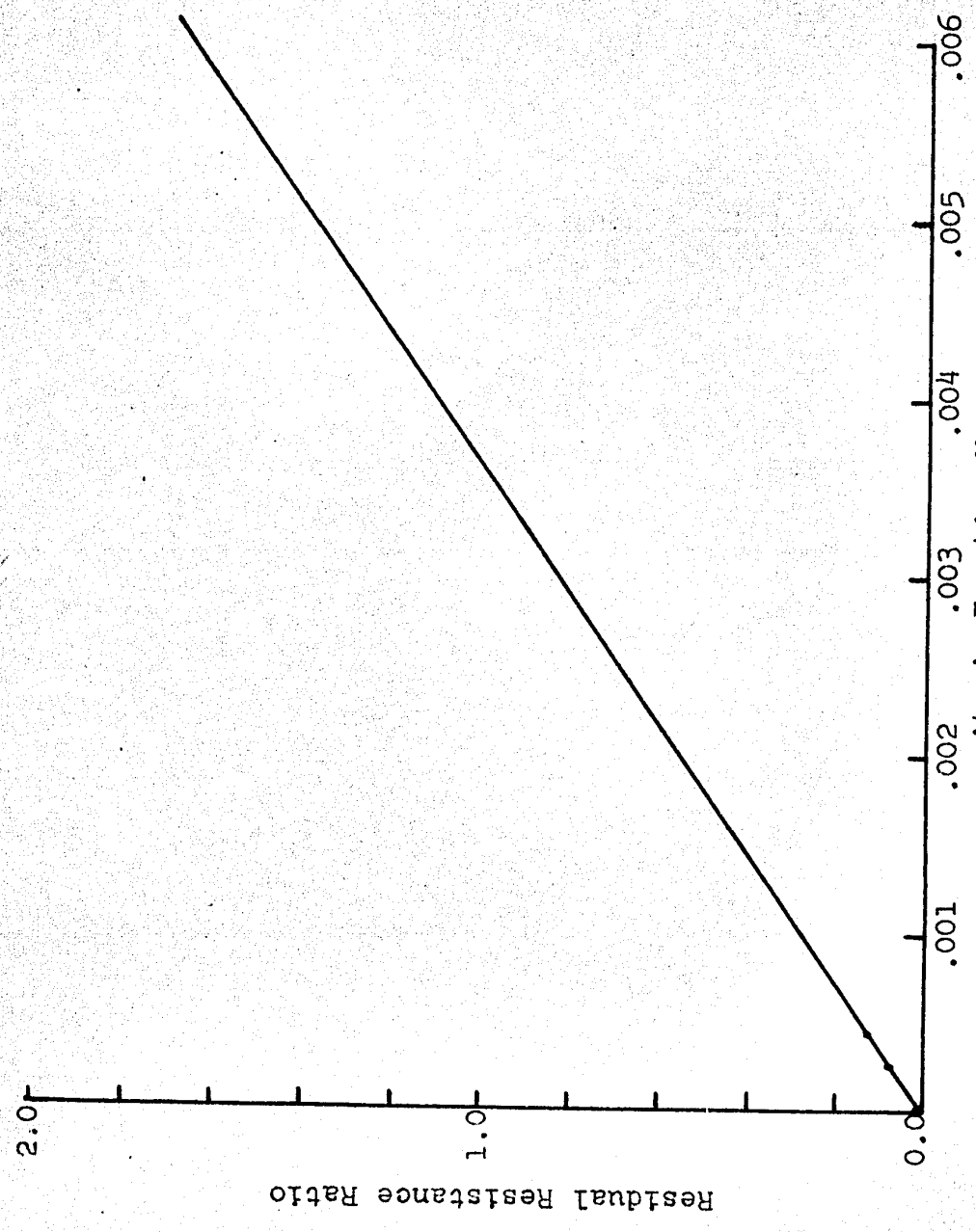

Fig. 2 Residual Resistance Ratios in Al-Mn
(Extrapolated values of Wallingford, 1960)

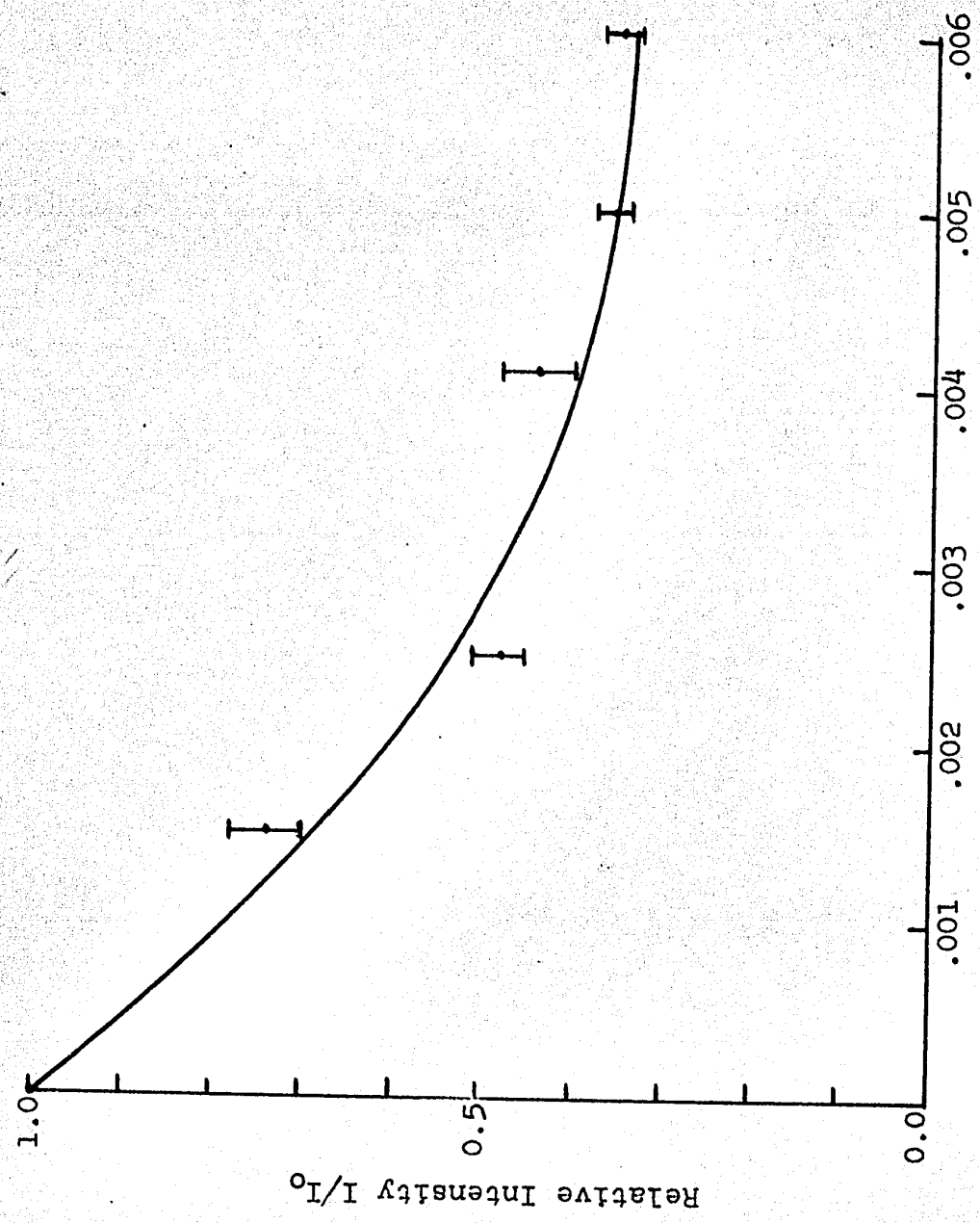

Fig. 3 Intensity of the Al27 Signal in Al-Mn

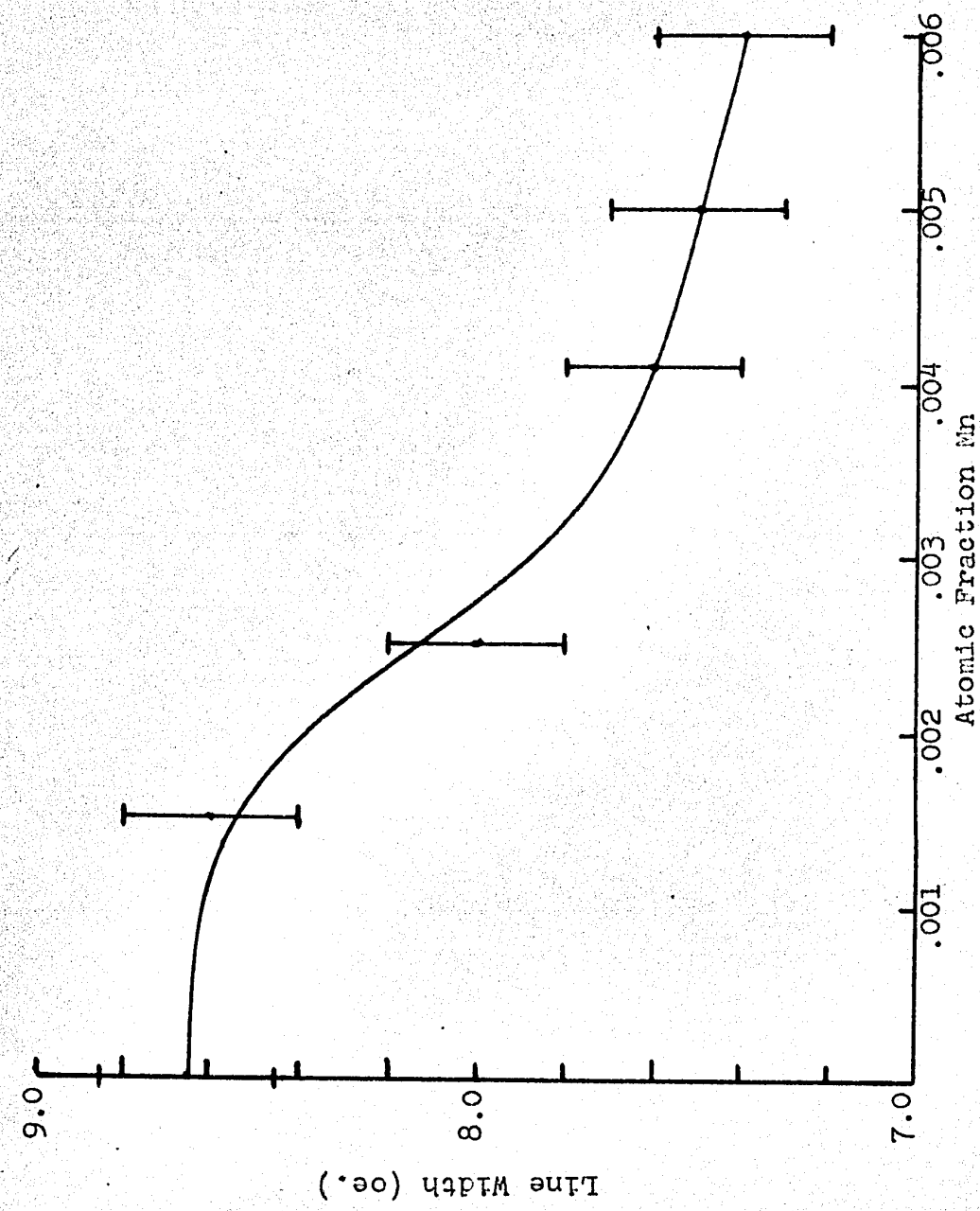

Fig. 4 Line Width in Al-Mn

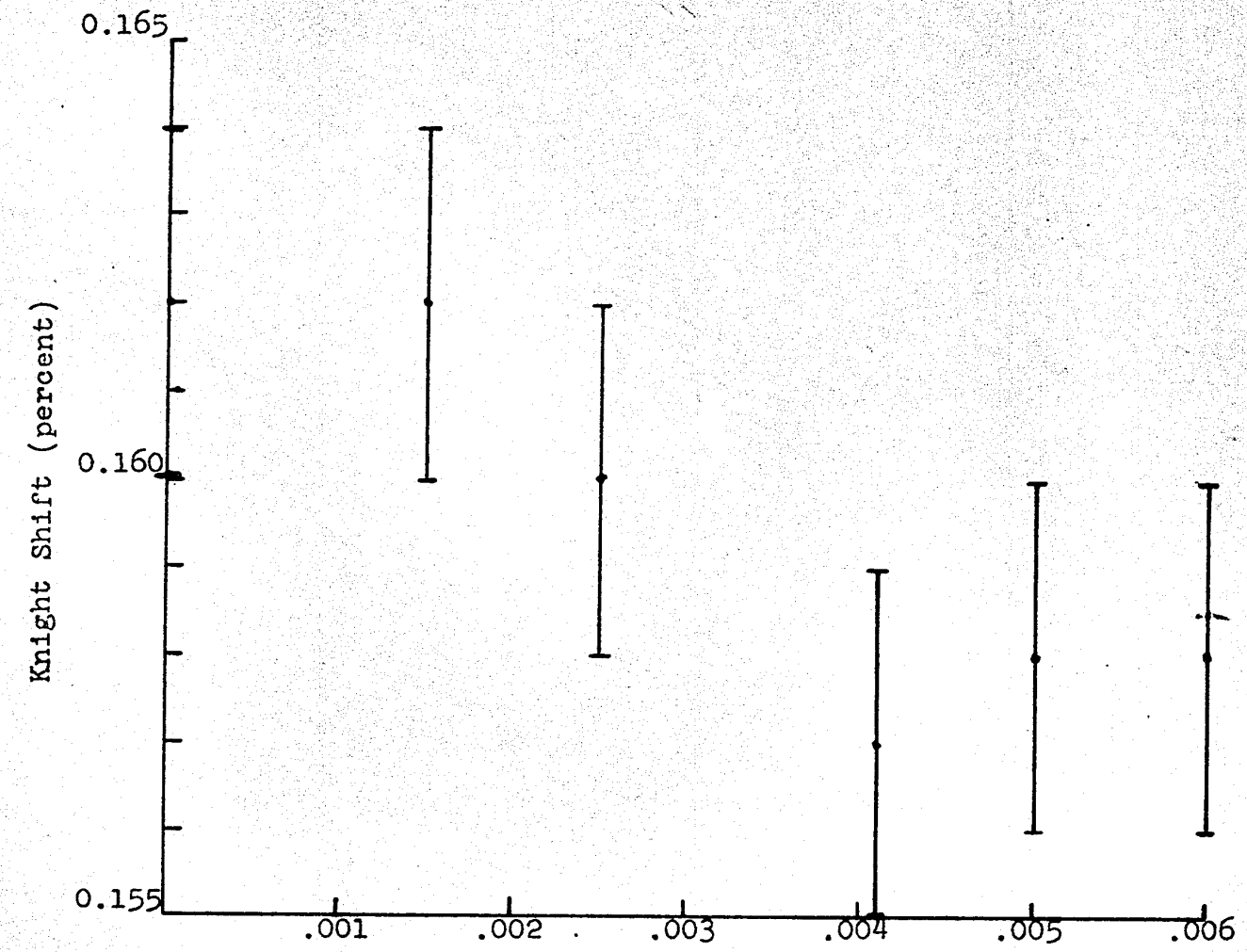

Fig. 5 Knight Shift in Al-Mn

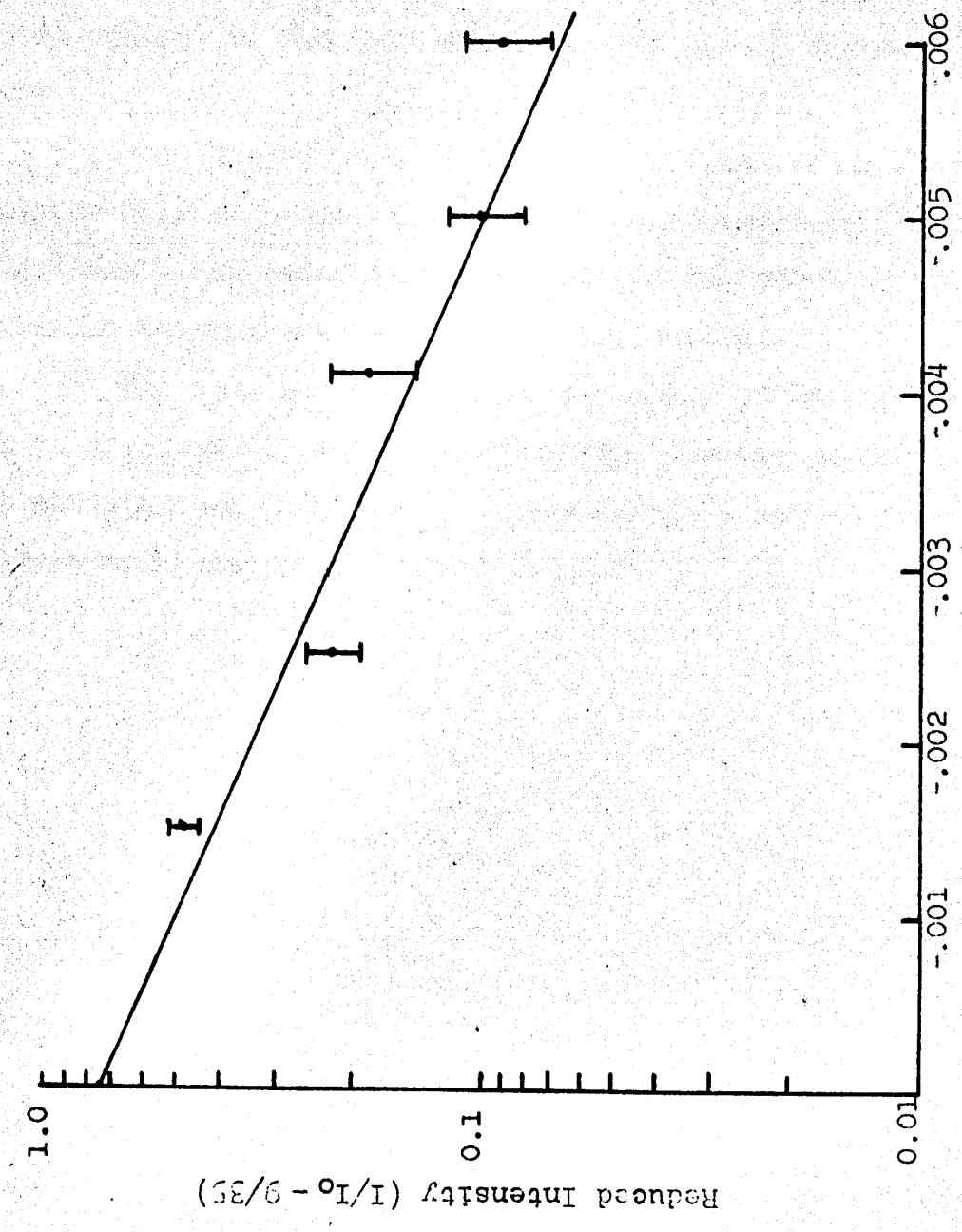

Fig. 6 Reduced Intensity in Al-Mn

and 0.161 ± .001 reported by Teotero (1955) and by Gutowsky and McCarvey (1952). This value is that obtained using a short time constant. The results shown for the alloys have been corrected for the long time constant effect discussed above.

The line width of 0.65 ± .2 oe. found by us in pure Al agrees well with the value of 0.5 oe. reported by Gutowsky and McCarvey. In both cases, line widths are taken to be the separation between the peaks of the derivatives.

The intensities are measured relative to the intensity observed in pure Al and show qualitative agreement with measurements on Al-Mg and Al-In alloys (Poulis, 1955). Discrepancies will be discussed below.

CHAPTER IV

DISCUSSION

4.1 - Intensity.

Bloembergen and Rowland (1953) have explained the large decrease in intensity which they observed in Cu-Mn alloys as follows. A nucleus with spin I has 2I + 1 equally spaced energy levels in a magnetic field. The n.m.r. signal therefore consists of 2I superimposed lines. If I 1/2, the nucleus has an electric quadrupole moment which interacts with an electric field gradient. This interaction perturbs the energy levels, removing the degeneracy. A first order perturbation calculation (Pound, 1950) for nuclei with half-integral spin in a polycrystalline sample shows that the m=1/2 to m=-1/2 transition, or central component, is unaffected. In a single crystal, the remaining components, or satellites, are symmetrically distributed in pairs about the central component. The splitting is found to be a function of the magnitude and of the orientation of the field gradient with respect to the direction of the magnetic field. In a powder, therefore, a distribution of frequencies is expected and a reduction in intensity is evident.

Quadrupole interactions do not exist in substances in which the electric field has cubic symmetry e.g. in pure well-annealed Al. The addition of an impurity disturbs the symmetry producing quadrupole effects. This disturbance is the basis of Bloembergen's and Rowland's explanation of the decrease in intensity. They postulate that the presence of

an impurity atom makes the signal unobservable from n solvent atoms surrounding the impurity, all others remaining unaffected. If c is the atomic fraction of solute, the relative intensity I/I_o should be proportional to $(1-c)^n$. A straight line of slope n should be found when log I/I_o is plotted against log (1 c). Such behaviour has been observed for the central component of the Cu^{63} resonance (Bloembergen and Rowland, 1953) and for the satellites of Al (Rowland, 1955). In the latter case, the contribution from the central component is subtracted from the total intensity. This contribution is expected, from theoretical considerations, to be 9/35, a value which has been experimentally confirmed. For the satellites therefore the quantity log $(I/I_o - 9/35)$ is plotted. With our results, a logarithmic plot of reduced intensity $(I/I_o - 9/35)$ shows the right behaviour (Fig. 6), but intensity is found to decrease much more rapidly in our alloys than in Al Mg or Al Zn. Rowland (1960) has shown that the disturbing effect of an impurity atom is due to a difference in charge between solute and solvent atoms with a small contribution due to a difference in size. It is expected that Al Mn should give the same results as Al Mg and Al Zn alloys.

It is known that, by cold working, a large number of dislocations, which do not anneal at room temperature (Cottrell, 1949), is produced in the specimens. This causes a decrease in intensity in pure cold worked Cu (Bloembergen

and Rowland, 1955) and an additional decrease in cold-worked Al-Mg alloys (Rowland, 1955). This additional decrease was found to disappear on annealing. To eliminate the effects of dislocations, Rowland used only well-annealed specimens. In our case, the solid solubility of Mn in Al is very small at room temperature. It was necessary in order to keep the Mn in solution to quench from the melt. Annealing of samples used for residual resistance measurements has revealed that in many cases some Mn is removed from solution by the annealing. Since we cannot anneal with confidence, it is necessary to accept the superimposed effects of both impurities and dislocations. This then would account for the more rapid decrease in intensity.

4.2 - Line width.

The addition of a paramagnetic impurity to a metal is expected to increase the dipolar and spin-exchange interactions and therefore the line width. A magnetic broadening proportional to applied field H and inversely proportional to temperature has indeed been observed by Chapman and Seymour (1958) in Cu-Mn alloys.

There is some evidence, however, that the magnetic behaviour of Al-Mn alloys differs fundamentally from that of Mg-Mn and Cu-Mn alloys. For example, at low temperatures Al-Mn does not have the large resistance anomalies observed in Mg-Mn (Hedgcock et al, 1960). Also, the magnetic susceptibility of Al-Mn alloys is temperature independent and the measured effective magneton number is 1.8 ± .4, much smaller

than the theoretical value of 5.9 and the observed value of 4.8±.5 found in Mg-Mn (Collings and Hedgcock, 1961).

It follows that no magnetic broadening of the n.m.r. line should be observed in Al-Mn alloys. One measurement at 4.2°K confirms the temperature independent behaviour of the line width. Hence we feel justified in assuming that there is no magnetic effect on the n.m.r. line.

Reif (1955) observed that, when the satellites were nearly obliterated by strains, the widths of the Br^{79} and Br^{81} resonances in a crystal of AgBr were smaller than in the unstrained crystal. He suggests that this narrowing of the line arises when intensity is removed from the middle of the central component and transferred to the wings. It would seem that the narrowing is due to quadrupole effects since straining the crystal has produced it but the mechanism suggested is not very satisfactory.

In Al-Mn (Fig. 4), the same narrowing occurs and is probably due to dislocations which are trapped in the metal by the presence of impurities. The concentration dependence would be explained by a larger number of dislocations being trapped in the metal by an increasing number of impurity centers. Hence the impurities affect the line width indirectly by locking in the dislocations which reduce the intensity and the width of the lines through quadrupole effects. The charge distortions introduced by the impurity atoms may also be responsible for the quadrupole narrowing of the line. A

complete annealing of the samples would clarify the situation but unfortunately, as we have already mentioned, it would remove the Mn from solid solution.

We may add finally that there is a fair amount of evidence that the Mn is still in solution. Firstly, the narrowing of the resonance line, if correctly explained above, and the intensity results would require the presence of the impurities. In the second place, measurements of residual resistance ratios both at the time of preparation of the samples and several months later indicate that in these specimens at least the Mn has remained in solid solution.

4.3 - Knight shift.

Fig. 5 indicates that the Knight shift does not vary appreciably with increasing concentration of Mn. The experimental values show a decrease which is just slightly greater than the experimental error.

According to Daniel (1959), a change in Knight shift, proportional to concentration, is expected on alloying. This change is caused by variations in the electron density produced by the presence of impurity atoms. A decrease in shift has been observed in Ag-Cd (Train, 1960) where the spin of the Ag nucleus is 1/2. In Al, the situation is complicated by the presence of quadrupole effects. Weeb (1961) has succeeded in separating the electron density and quadrupole effects in Al-Mg and Al-Zn. The fractional change in Knight shift per atomic percent solute $\left(\frac{1}{c}\frac{\delta K}{K}\right)$ due to a change in the

electron density if less than 0.1 whereas the quadrupole shift is an order of magnitude or more greater. We observe a value of 4 for this quantity. It is believed that the decrease in Knight shift is due largely to quadrupole interactions. The magnitude of the decrease may indicate again the importance of dislocations.

We would like to point out finally an interesting effect of dislocations on the Knight shift in pure Al and in the Al Mn alloys which to our knowledge has not been reported in the literature. Immediately after filing, an abnormal decrease in resonance frequency of about 1.5 kc/sec. was observed. This is considerably larger than the decrease plotted in Fig. 5. This decrease was found to disappear after about 2 weeks in pure Al and after about 5 weeks in the alloys. We believe that it can be accounted for as follows. In the pure metal, the dislocations are known to disappear quickly at room temperature. In the alloys, the impurity atoms lock in the dislocations and the annealing is much slower. In fact, intensity measurements indicate that annealing is not complete. It is of interest to point out that the change in frequency observed after filing and on alloying are in the same direction. In support of our interpretation, we have verified that annealing a pure Al sample at 450 C for 3 to 4 hours completely removes the abnormal decrease.

CHAPTER V

CONCLUSIONS

The values of 0.162±.002% for the Knight shift and of 8.6±.2 oe. for the line width are in good agreement with values reported elsewhere.

The decreases in intensity, line width and Knight shift observed are accounted for by nuclear electric quadrupole effects. The inability to anneal the specimens makes impossible a proper evaluation of the contribution of impurities and dislocations to these effects.

Confirmation of the non magnetic behaviour of the Al Mn alloys has been obtained. Further measurements should be taken at 4.2°K in order to verify this. It would be interesting also to get quantitative measurements of the annealing process in pure Al and in the alloys using the abnormal shift found immediately after filing.

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