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HAL Id: jpa-00215655
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Submitted on 1 Jan 1974

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NUCLEAR MAGNETIC RESONANCE IN LIQUID MANGANESE

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Résumé. — Nous reportons des mesures du déplacement de Knight \( \kappa^{55} \) et du temps de relaxation spin-réseau \( T_1 \) pour \(^{55}\)Mn, dans Mn liquide et dans les phases solides \( y \) (c. f. c.) et \( \delta \) (c. b. c.) sur le domaine de température \( 1350 \leq T \leq 1575 \) K. La valeur de \( \kappa^{55} \) dans Mn liquide à 1 525 K est de \(-0.820 \pm 0.005 \) % et celle de \( 1/T_1 \) est de \( 2.2 \pm 0.1 \times 10^4 \) s\(^{-1}\). Une analyse détaillée de la dépendance en température des déplacements de Knight et des susceptibilités magnétiques \( (\gamma) \) montre que la susceptibility de spin \( (\gamma) \) contribue pour 75 \% environ à la susceptibility totale, le reste étant principalement dû au paramagnétisme orbital \( (x_{\text{orb}}) \). Les valeurs de \( x_{\text{orb}} \) dans Mn liquide et solide \( (\delta - \text{Mn}) \) sont à \( \sim 2 \) \% près égales, et toutes les deux dépassent de 10 \% environ celles de \( y - \text{Mn} \). On déduit un couplage hyperfin de la polarisation d'électrons de couches internes de \(-223 \pm 22 \) kG/magnétone de Bohr, pour toutes les trois phases. Les vitesses de relaxation dans les phases liquides et solides s'accordent avec une relaxation de type Korringa par électrons d'itinérants.

Abstract. — We report measurements of the Knight shift \( \kappa^{55} \) and spin-lattice relaxation time \( T_1 \) for \(^{55}\)Mn in liquid Mn and in the solid \( y \) (FCC) and \( \delta \) (BCC) phases over the temperature range \( 1350 \leq T \leq 1575 \) K. The value of \( \kappa^{55} \) in liquid Mn at 1 525 K is \(-0.820 \pm 0.005 \) \% and \( 1/T_1 \) is \( 2.2 \pm 0.1 \times 10^4 \) s\(^{-1}\). Detailed analysis of the temperature dependent Knight shifts and magnetic susceptibilities \( (\gamma) \) show that the d-spin susceptibility \( (\gamma) \) is responsible for roughly 75 \% of the total susceptibility, the remainder being due mainly to orbital paramagnetism \( (x_{\text{orb}}) \). The values of \( x_{\text{orb}} \) in liquid and solid \( \delta - \text{Mn} \) are equal to within about 2 \% and both are greater than in \( y - \text{Mn} \) by about 10 \%. Core polarization hyperfine couplings in the range \(-225 \pm 25 \) kG/Bohr magneton are deduced for all three phases. The relaxation rates in liquid and solid are consistent with Korringa relaxation by itinerant d-electrons.

1. Introduction. — Although the electronic and magnetic properties of liquid transition metals have received considerable recent attention [1-4] there have been no nuclear magnetic resonance (NMR) studies of these interesting systems. The absence of NMR data is undoubtedly related to experimental difficulties associated with the high melting points and chemical reactivity of the transition metals.

Because of its relatively low melting point \( (1.517 \) K) and the large nuclear moment and abundance of \(^{55}\)Mn, manganese is the most favorable transition metal for study in the liquid state. In addition, recent data [5] obtained for dilute \(^{55}\)Mn NMR in liquid Cu and Al hosts provide interesting comparisons between the local magnetic properties of the concentrated metal and impurity states. In the present work we report data for the \(^{55}\)Mn Knight shift \( \kappa^{55} \) and spin-lattice relaxation rate \( (1/T_1) \) in the solid \( y \) (FCC) and \( \delta \) (BCC) phases and in the liquid over the temperature range \( 1350 \leq T \leq 1575 \) K.

2. Experimental. — Samples used for these experiments were prepared from electrolytically deposited \( \alpha - \text{Mn} \) which was pulverized in an argon atmosphere and mixed with high purity \( \text{Al}_2\text{O}_3 \) to provide rf penetration. Chemical analysis of the starting material revealed less than 10 ppm of metallic impurities and less than 200 ppm of oxygen. For NMR experiments, the Mn-\( \text{Al}_2\text{O}_3 \) mixture was heated in a closed tube of high purity recrystallized \( \text{Al}_2\text{O}_3 \) containing argon gas and a Ti getter. Oxidation of the sample during experimental runs was minimized by using high purity, water free argon and by carefully degassing all ceramic components before each run. The main effect of small amounts of \( \text{O}_2 \) was observed to be stabilization of the \( y \) phase against transformation to \( \beta - \) and \( \delta - \text{Mn} \).

NMR was observed with a single Pt coil placed around the \( \text{Al}_2\text{O}_3 \) sample container. All data were taken at a frequency of 16.35 MHz using conventional coherent pulsed NMR techniques.

Knight shift results are plotted in figure 1 as a function of temperature. The reference field for these measurements was determined from the value \( \gamma^{55} = 1.0500 \) kHz/G for the \(^{55}\)Mn gyromagnetic ratio [6]. The observed shifts are negative throughout the temperature range investigated indicating that d-electron core-polarization effects dominate the

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local magnetic hyperfine field. Within each phase the shift becomes increasingly negative on heating. At the $\gamma \to \delta$ transition, the shift becomes more negative whereas at the melting transition, the change is in the positive direction. The data were completely reversible on heating and cooling from which we conclude that progressive oxidation of the samples was negligible.

Spin-lattice relaxation rates are given in figure 1. We found $1/T_1$ to be nearly constant throughout the range of observation. The data in $\delta$ and liquid phases are consistent with a constant value of $(T_1 T)^{-1}$ whereas $(T_1 T)^{-1}$ tends to decrease slightly in $\gamma$-phase.

3. Discussion. — Knight shift and susceptibility ($\chi$) data [7] are correlated by means of a $k^{55}$ versus $\chi$ plot [8] in figure 2. This plot can be analyzed in terms of the following decompositions of $\chi$ and $k^{55}$.

$$\chi = \chi_s + \chi_{\text{dis}} + \chi_d(T) + \chi_{\text{orb}}$$

$$k^{55} = \kappa_s + \alpha \chi_d(T) + \beta \chi_{\text{orb}}$$

where $\chi_s$ and $\kappa_s$ are, respectively, the s-electron susceptibility and shift, $\chi_{\text{dis}}$ is the diamagnetic susceptibility and $\chi_{\text{orb}}$ is the d-electron orbital susceptibility. The coefficients $\alpha$ and $\beta$ are proportional to the core-polarization and orbital hyperfine fields, respectively. The orbital and d-spin susceptibilities and shifts are determined by assuming (i) a numerical value for $\kappa_s$, (ii) a calculated value for $\beta$, (iii) that $\chi_s + \chi_{\text{dis}}$ is negligible compared with $\chi_d(T)$ and $\chi_{\text{orb}}$ and (iv) that $\chi_d$ is the only temperature dependent contribution to $\chi$.

The slope $dk/d\chi$ given by the experimental results corresponds to $\alpha = 40 \pm 4$ mole/emu or a hyperfine field $H_{hf} = -223 \pm 22$ kG per Bohr magneton. Taking the values $\kappa_s = +0.2$ % (typical for this part of the periodic table) and $\beta = 65$ mole/emu [9] we find by extrapolation of the $\delta$-phase data that $\kappa_{\text{orb}} = 1.0$ % and $\chi_{\text{orb}} = 0.15 \times 10^{-3}$ emu/mole. Thus, orbital paramagnetism accounts for 20-25 % of the total susceptibility, the remainder being the temperature dependent spin susceptibility.

The $k^{55} - \chi$ analysis suggests close similarity between the liquid and $\delta$-Mn. The small displacement of the liquid data relative to $\delta$-Mn could be due to a small increase in $\chi_{\text{orb}}$ or, alternatively, to a $\sim 1$ % increase in $\chi_d$ accompanied by a slight decrease in $\alpha$. In either case we find little change in $\chi_d$ on melting. At the $\gamma \to \delta$ transition, on the other hand, $\chi_d$ increases by $\sim 10$ %. This result suggests, indirectly, that the liquid structure resembles more the 8 near-neighbor coordination of the BCC structure than it does the close-packed arrangement of the FCC phase.

The observed spin-lattice relaxation rates are consistent with expectations for relaxation via itinerant d-electrons. The coupling to d-electron spins by the core-polarization hyperfine field, for example, gives a relaxation rate in a cubic metal described by

$$\left(\frac{1}{T_1}\right)_d = \left(\frac{4 \pi k}{\hbar}\right) \left(\frac{\gamma_n}{\gamma_s}\right)^2 \kappa_d T$$

where $\gamma_n$ and $\gamma_s$ are, respectively, the electronic and nuclear gyromagnetic ratios and $q$ is a parameter characterizing the relative proportion of $\Gamma_3$ and $\Gamma_5$ d-orbitals at the Fermi level. If all five d-orbitals contribute equally ($q = 0.2$), we find for $\delta$-Mn at
NUCLEAR MAGNETIC RESONANCE IN LIQUID MANGANESE C4-339

Table I
Results of $\chi^{55}$ versus $\chi$ analysis for liquid Mn, solid $\gamma$- and $\delta$-Mn, and dilute (4 at. %) Mn in liquid Al and Cu.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\chi_d$ ($10^{-3}$ emu/mole)</th>
<th>$\chi_{orb}$ ($10^{-3}$ emu/mole)</th>
<th>$H_{sf}$ (kG/Bohr magnet.)</th>
<th>$1/T_1$ ($10^4$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Mn</td>
<td>1 400</td>
<td>0.450 ± 0.020</td>
<td>0.140 ± 0.020</td>
<td>223 ± 22</td>
</tr>
<tr>
<td>$\delta$-Mn</td>
<td>1 450</td>
<td>0.485 ± 0.014</td>
<td>0.154 ± 0.014</td>
<td>234 ± 17</td>
</tr>
<tr>
<td>l-Mn</td>
<td>1 525</td>
<td>0.503 ± 0.011</td>
<td>0.147 ± 0.011</td>
<td>220 ± 14</td>
</tr>
<tr>
<td>Al : Mn (*)</td>
<td>1 250</td>
<td>0.94</td>
<td>0.13</td>
<td>85</td>
</tr>
<tr>
<td>Cu : Mn (*)</td>
<td>1 350</td>
<td>2.63</td>
<td>0</td>
<td>66</td>
</tr>
</tbody>
</table>

(*) Reference [5].

1450 K the value $(1/T_1)_d = 2.8 \times 10^4$ s$^{-1}$. Inclusion of electron-electron effects would decrease this value by perhaps a factor of two while a contribution from an orbital relaxation process would increase the value of $1/T_1$. Thus, while there is not sufficient information to effect a quantitative analysis of the $T_1$ data, the observed value of $2.05 \pm 0.1 \times 10^4$ s$^{-1}$ is in reasonable agreement with theory. The relaxation behavior in liquid Mn is very similar to solid $\gamma$- and $\delta$-Mn suggesting that the effective value of $q$, the orbital relaxation and the electron-electron effects are relatively unchanged on melting.

Finally, it is interesting to compare the susceptibility, hyperfine couplings and relaxation rates obtained for $\gamma$, $\delta$- and liquid Mn with those determined from recent NMR experiments on dilute Mn$^{55}$ in liquid Al and Cu [5]. These comparisons are summarized in Table I. The relaxation rates of Mn and Al : Mn are quite similar as are the values of $\chi_{orb}$. The value of $\chi_d$ is bigger in Al : Mn a by factor $\sim 2$ whereas the hyperfine coupling is a factor $\sim 3$ bigger in concentrated Mn. The value of $\chi_{orb}$ and the relaxation behavior of Mn and Al : Mn, however, contrast sharply with Cu : Mn where the formation of a local moment leads to vanishing $\chi_{orb}$ and an order of magnitude higher relaxation rate. These results serve to emphasize the itinerant character of the d-electrons in Al : Mn and pure Mn.

4. Conclusions. — We find that the magnetic susceptibility and Knight shift of liquid Mn are dominated by a $\sigma$-spin contribution which is essentially unchanged on melting BCC $\delta$-Mn. The orbital susceptibility also changes little on melting. These results suggest that the form of the d-electron density of states in the liquid closely resembles that of the BCC solid structure. A discernibly smaller ($\sim 10 \%$) spin susceptibility was found for FCC $\gamma$-Mn but the magnitude of this change indicates the absence of major alteration of the density of states at the $\gamma \to \delta$ transition. Nuclear relaxation results are in accord with fully itinerant d-electrons and the spin dynamics of Al : Mn and Mn are found to be rather similar.

Acknowledgments. — The authors are indebted to V. J. Albano for providing the electrolytic manganese used in these experiments. We also thank G. F. Brennert for expert technical assistance.

References