

above are in esu units, and one should remember that  $|\nabla E| \cong 10^5 |E|$  in these experiments. These values are in order-of-magnitude agreement with preliminary theoretical calculations based on crystalline-field parameters.

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### NUCLEAR MAGNETIC RESONANCE IN PLATINUM\*

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We present here pulsed nuclear magnetic resonance (NMR) measurements on Pt<sup>195</sup> in platinum metal, in the course of which we observed anomalies in the linewidth and the spin-lattice relaxation time  $T_1$ . Since all the NMR properties of platinum metal depend intimately on the electron-nucleus interactions, an experimental investigation of these properties may throw light on this little-understood case of paramagnetism in the transition metal series.

In the temperature range from 0.02°K to 2°K, where  $T_1$  is much longer than the spin-spin relaxation time  $T_2$ , the following anomalies are observed:

(1) The resonance line, which is inferred from the observed free-precession decay function  $\exp(-t/T_2)$  to be very nearly Lorentzian, exhibits a net narrowing. Experimental data demonstrate the presence of three distinct spin-spin interactions: classical dipolar, pseudodipolar,<sup>1</sup> and indirect exchange.<sup>2</sup> The two dipolar couplings both broaden the line, the second being slightly stronger than the first. The dominant indirect exchange coupling between like spins reduces the resulting linewidth by an order of magnitude. This is believed to be the first case of exchange narrowing reported for NMR. The previously observed exchange broadening<sup>1,2</sup> is absent here, since platinum contains only one species of nuclear spin.

(2) Experimental values of the quantity  $T_1T$ , theoretically temperature independent,<sup>3</sup> are plotted vs temperature  $T$  in Fig. 1 and are shown

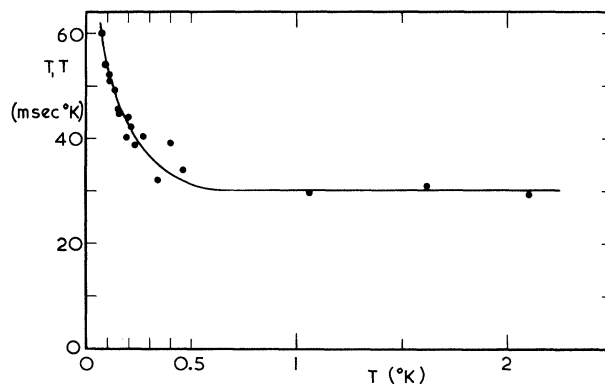


FIG. 1.  $T_1T$  vs  $T$  for Pt<sup>195</sup> in platinum metal in a field of 490 gauss. The constant value of  $T_1T$  above 1°K is 30 msec °K.

to undergo a significant increase below 0.5°K. Rough measurements<sup>4</sup> in the region  $0.02^\circ\text{K} \leq T \leq 0.05^\circ\text{K}$  indicate a still increasing value of  $T_1T$ . The observed deviation corresponds to a weakening of the relaxation mechanism.

The analysis of spin-spin interaction contributions has been made<sup>5</sup> using two pieces of experimental data: (a) the value of  $T_2$ , and (b) the field dependence of  $T_1$ .  $T_2$  was measured from free-precession signals at 0.02°K in a field of 100 gauss and with spin echoes at 1°K in fields of 490 and 1840 gauss, giving a value of  $1.05 \pm 0.1$  msec in all cases. For an exchange-narrowed line, Anderson and Weiss<sup>6</sup> derive a free-precession decay function  $\exp(-t/T_2)$  with  $T_2 = \omega_e / \langle \Delta\omega^2 \rangle$ .

Here  $\langle \Delta\omega^2 \rangle$  is the second moment<sup>7</sup> of the line and  $\omega_e$  is a frequency of the order of the nearest neighbor indirect exchange coupling constant  $J$ . Calculation of the fourth moment  $\langle \Delta\omega^4 \rangle$  gives the relation<sup>6</sup>  $\omega_e = 2.9J$  for Pt<sup>195</sup> in fcc platinum metal. Combining this relation with the measured value of  $T_2$  in the equation above gives  $\langle \Delta\omega^2 \rangle = 2.8 \times 10^3 J$ .

A second equation relating  $\langle \Delta\omega^2 \rangle$  and  $J$  may be found from a theoretical interpretation of data on the field dependence of  $T_1$ . These data were obtained by a field-switching method<sup>8,9</sup> and are shown in Fig. 2. The solid curve drawn is an interpretation of the data with the theoretical function  $T_1(H_0)/T_1(\infty) = [H_0^2 + H_L^2]/[H_0^2 + 2H_L^2]$  given by Redfield<sup>10</sup> and by Hebel and Slichter.<sup>9</sup>  $H_L$  is an effective local field defined by the equation

$$H_L^2 = \frac{5}{3} \langle \Delta\omega^2 \rangle / \gamma^2 + [I(I+1)/\gamma^2 N] \sum_{j < k} J_{jk}^2,$$

where  $\gamma$  is the nuclear gyromagnetic ratio and  $N$  is the number of spins per cc. Inserting the experimental value  $H_L^2 = 12.5$  gauss<sup>2</sup> and evaluating the sum for nearest neighbor exchange only, one obtains the desired relation:  $1.67 \langle \Delta\omega^2 \rangle + 1.5 J^2 = 4.13 \times 10^8 \text{ sec}^{-2}$ .

When the two equations involving  $J$  and  $\langle \Delta\omega^2 \rangle$  are combined, the resulting quadratic equation in  $J$  is solved to give  $J = 1.52 \times 10^4 \text{ sec}^{-1}$ , corresponding to  $\langle \Delta\omega^2 \rangle = 4.22 \times 10^7 \text{ sec}^{-2}$ . This second moment value is to be compared with the calculated classical dipolar value  $\langle \Delta\omega^2 \rangle_{cl} = 6.1 \times 10^6 \text{ sec}^{-2}$ . The increase in  $\langle \Delta\omega^2 \rangle$  is attributed to a pseudodipolar term 1.6 times stronger than the classical dipolar coupling. The associated broadening effect is counteracted by the strong

indirect exchange  $J$ , so that the actual half-power linewidth is one-eighth of what it would be in the absence of exchange.

Certain measures have been taken to ensure that the observed temperature dependence of  $T_1 T$  is a genuine effect.  $T_1$  measurements were carried out by the two-pulse method.<sup>11</sup> Below 1°K temperature, drifts were sufficiently slow so that a unique temperature could be assigned to each of these measurements, as reflected by the purely exponential character of the relaxation plots. The sample temperature was calculated from the free-precession signal amplitude corresponding to the equilibrium nuclear magnetization with the help of Curie's law. The validity of this law for Pt<sup>195</sup> was checked over the range from 0.04°K to 1°K by comparison with the magnetization of Na<sup>23</sup> nuclei in a sample consisting of platinum and sodium particles mixed in oil. Moreover, a determination of the  $T_1 T$  value of sodium at 0.07°K under identical experimental conditions gave good agreement with the high-temperature results of Anderson and Redfield.<sup>8</sup>

In seeking a physical explanation for the observed variation in  $T_1 T$ , it is perhaps worth while to recall that for spin-lattice relaxation caused by electrons obeying Fermi statistics, Korringa's theory<sup>3</sup> predicts a constant  $T_1 T$  value over the range  $\mu_N H_0 / k \approx 10^{-5} \text{ °K} \ll T \ll T_{\text{Fermi}}$ , where  $\mu_N$  is the nuclear magnetic moment and  $k$  is Boltzmann's constant. Here our temperatures are well within these limits. Among the possible effects due to paramagnetic impurities<sup>12</sup> are a field-dependent line broadening, which is not observed here, and a contribution to the spin-lattice relaxation rate, the temperature dependence of which is incompatible with our  $T_1$  data. Spectroscopic analysis shows that our platinum specimens contain a maximum of 0.002% iron impurities. Under the circumstances, then, one may suspect that the  $T_1$  anomaly is connected with the intrinsic properties of the  $s-d$  electron configuration in platinum metal. The field dependence of this effect is currently under investigation.

We have also determined the resonant frequency of Pt<sup>195</sup> from free-precession signals in a field of 569 gauss and have found it to be constant from 0.07°K to 1°K. The shift  $\Delta\omega/\omega_0 = -(4.04 \pm 0.04)\%$ , calculated with the help of the moment determination of Proctor and Yu,<sup>13</sup> is compatible with the results of Rowland<sup>14</sup> at 77°K. A mechanism has been suggested<sup>15</sup> for this negative frequency shift which invokes the polariza-

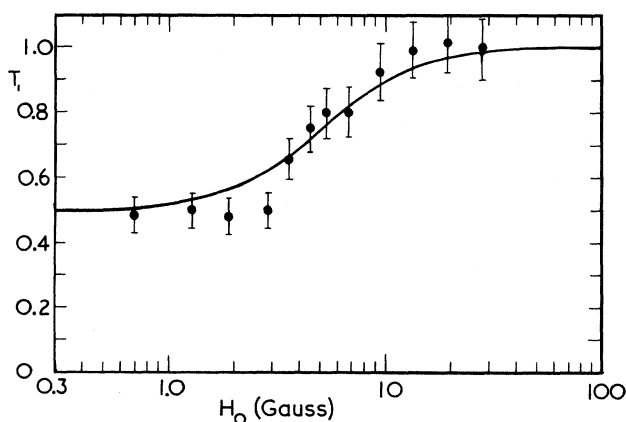


FIG. 2.  $T_1$  vs applied field  $H_0$  at a temperature  $T = 0.15^\circ\text{K}$ .  $T_1$  is in units of its high-field value (0.31 sec). The solid curve is a theoretical function stated in the text.

tion of the core- $s$  electrons by the unpaired  $d$  electrons. It is somewhat surprising to find constant values of frequency shift and linewidth in the temperature range where  $T_1T$  is varying.

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## SUPERCONDUCTIVITY OF IRIIDIUM

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We have discovered that very pure iridium is a superconductor with a zero-field transition temperature of  $0.140^\circ\text{K}$ .<sup>1</sup> It is known that the existence in a superconductor of an impurity such as iron drastically lowers the superconducting transition temperature, if, and only if, the iron impurity possesses a localized magnetic moment.<sup>2</sup> Localization of the Fe moment has been found to be a function of the number of valence electrons possessed by the host metal.<sup>3</sup> Molybdenum and iridium are two metals in which Fe, if present as an impurity, would possess a localized magnetic moment. The present discovery and the recent discovery that Mo is a superconductor<sup>4</sup> suggest that failure of many metals to exhibit superconductivity, even when cooled to ultra-low temperatures, could be due to insufficient purity. Mo and Ir are the first transition metals in which Fe, if present as an impurity, would possess a magnetic moment, which have been found to be superconductors. This suggests that superconductivity is probably a more widespread phe-

nomenon than presently believed.

The metal iridium has previously been reported to be nonsuperconducting down to  $0.1^\circ\text{K}$ .<sup>5</sup> However, with the above considerations in mind, high-purity Ir was prepared in a way similar to that used for Mo.<sup>4</sup> Three specimens of Ir were placed in an argon arc furnace and were maintained in the liquid phase for 12 minutes. The resulting pellets were approximately spherical in shape with an average diameter of about 3 mm. The starting material was Johnson Matthey high-purity Ir. The manufacturer's analyses showed that there was no more than 2 parts per million of any other element present in the starting material.

Temperatures below  $1^\circ\text{K}$  were produced by the magnetic cooling method. Thermal contact between the salt and the specimen was achieved by cementing the pellets (GE Adhesive No. 7031) to a slotted copper bar which in turn was in contact with a paramagnetic salt pill. Two Speer 470 ohm- $\frac{1}{2}$  watt resistors were also cemented to the