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Direct Observation of Mn^{55} NMR in Antiferromagnetic $CsMnF_3$†

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The direct nuclear magnetic resonance (NMR) of the Mn^{55} nuclei in the hexagonal antiferromagnet $CsMnF_3$ has been observed in the frequency range between 250 and 650 Mc/sec. The very strong temperature and field dependence of the NMR frequency in the liquid-helium temperature range can be explained by the nuclear-electron coupling theory of NMR in magnetic materials developed by de Gennes. The results of the NMR experiments are in good agreement with the two-sublattice model proposed for $CsMnF_3$ by Lee. The NMR frequency extrapolated to infinite nuclear temperature was found to be 666 Mc/sec. This suggests a zero-point spin-wave reduction of $3.0\pm1.0\%$; Davis's calculation predicts a 4.36% reduction in $\langle S\rangle$.

INTRODUCTION

THERE is exhibited in $CsMnF_3$ a magnetic transition from the paramagnetic state to the antiferromagnetic state at a temperature of 55°K.[1] Crystallographic studies[2] indicate that $CsMnF_3$ has the same structure as the hexagonal form of $BaTiO_3$ (Fig. 1). The Mn^{2+} ions are situated in two inequivalent sites; one-third of the Mn^{2+} ions ($Mn_{(1)}$) are in sites with a point symmetry of $\bar{3}m(D_{3d})$ while the remaining two-thirds ($Mn_{(2)}$) are in sites with a point symmetry of $3m(C_{3v})$. Below the Neél temperature the magnetic moments associated with the Mn^{2+} ions lie in the plane perpendicular to the hexagonal c axis; the magnetic ordering can be viewed as an antiferromagnetic stacking of sheets of $Mn_{(1)}$ ions with two sheets of $Mn_{(2)}$ ions inserted between the sheets of $Mn_{(1)}$ ions in such a way that the spins of nearest-neighbor $Mn_{(1)}-Mn_{(2)}$ ions are antiferromagnetic. This spin arrangement has been confirmed by torsion experiments, antiferromagnetic resonance (AFR) experiments,[1] and neutron diffraction studies.[3] The results of the torsion experiments show that the anisotropy energy of the spins in the (00.1) plane is very small. Lee *et al.*[1] could account for all of the in-plane anisotropy of their samples by using a 1-Oe sixfold anisotropy energy. The magnetic spins are confined to the (00.1) plane by a large uniaxial anisotropy ($H_1=7500$ Oe); the uniaxial anisotropy is caused by the dipole-dipole interaction between spins and a single-ion-type anisotropy arising from the configuration of the fluorine octahedra surrounding a Mn^{2+} ion. The major contribution to the uniaxial anisotropy comes from the dipole-dipole interaction.

As a consequence of the low in-plane anisotropy, $CsMnF_3$ has a low-lying AFR mode. The contribution of the hyperfine interaction of the magnetic electrons with the Mn^{55} nuclei to the AFR frequency of this mode should be appreciable since the Mn^{55} nucleus is 100% abundant and has a large hyperfine interaction with the electrons. The dependence of the AFR frequency on temperature for temperatures well below the Neél temperature should reflect the temperature dependence of the nuclear magnetization. These expectations were confirmed by the AFR experiments of Lee.[1]

The importance of the contribution of the hyperfine interaction to the AFR frequency indicates that electronic excitation spectrum and the nuclear excitation spectrum are very strongly mixed and that the nuclear-electron coupling theory of NMR in magnetic materials developed by de Gennes *et al.*[4] should be used to explain the NMR results for $CsMnF_3$. The admixture of the electronic excitation spectrum into the nuclear spectrum is accomplished by coupling the nuclei via the Suhl-Nakamura indirect interaction.[5] The result of the theory is that for low temperatures and for magnetic materials in which the range of the Suhl-Nakamura interaction is large, cooperative effects in the nuclear system become important. Nuclear spin waves become well-defined excitations at temperatures for which the nuclear magnetization is far from saturation; the $\mathbf{k}=0$ excitation (NMR frequency) occurs at a frequency that is less than the hyperfine-field frequency. The depression of the frequency for NMR has been observed by direct NMR methods in the antiferromagnets $KMnF_3$,[6] $RbMnF_3$,[7] and $CsMnF_3$.

THEORY

To obtain expressions for the AFR and NMR frequencies for $CsMnF_3$ we take as the magnetic energy for the nuclear-electron system,[4]

$$U=\lambda\mathbf{M}_1\cdot\mathbf{M}_2-\mathbf{H}_0\cdot M_1-\mathbf{H}_0\cdot M_2 +\tfrac{1}{2}(K_1/M_0^2)(M_{1z}^2+M_{2z}^2)-\alpha\mathbf{m}_3\cdot\mathbf{M}_1-\alpha m_4\cdot\mathbf{M}_2\,, \quad (1)$$

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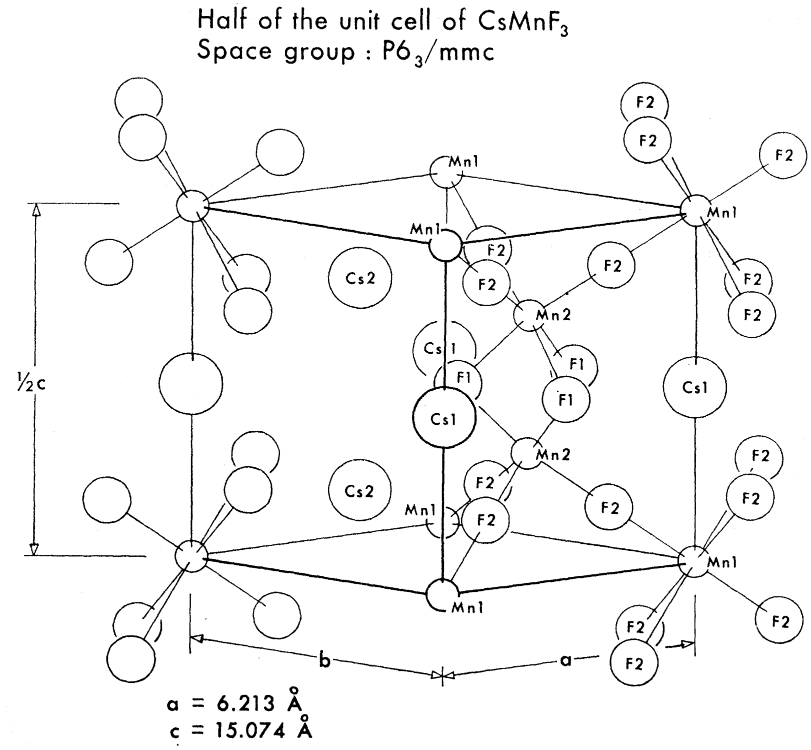

FIG. 1. Half of the chemical cell of CsMnF$_3$.

where $\mathbf{M}_{1,2}$ and $\mathbf{m}_{3,4}$ are the electronic and the nuclear sublattice magnetizations, respectively, α is proportional to the effective hyperfine coupling constant, K_1 is a uniaxial anisotropy, $\mathbf{H}_0$ is the applied dc magnetic field, and λ is the antiferromagnetic exchange constant. Strictly speaking, CsMnF$_3$ is a four-sublattice system. However, calculation shows that on a four-sublattice model two of the resulting AFR modes are exchange modes and the remaining two are equal to the two modes that one obtains from Eq. (1) with α set equal to $\alpha_1/3+2\alpha_2/3$, where α_1 and α_2 are the hyperfine coupling constants of the Mn$_{(1)}$ ion and Mn$_{(2)}$ ions, respectively.

To solve Eq. (1) for its eigenfrequencies, we transform to polar coordinates (see Fig. 2), expand Eq. (1) to second order in small quantities around the equilibrium configuration, and use the equations of motion for $\delta\theta_i$ and $\delta\phi_i$ to construct the 8×8 resonance matrix, obtaining

$$\frac{1}{\Gamma}\frac{d\delta\phi_i}{dt}=-\frac{1}{M_i\sin\theta_{i0}}\frac{\partial U}{\partial\delta\theta_i},\qquad \frac{1}{\Gamma}\frac{d\delta\theta_i}{dt}=\frac{1}{M_i\sin\theta_{i0}}\frac{\partial U}{\partial\delta\phi_i},\qquad i=1,2 \tag{2}$$

$$\frac{1}{\gamma}\frac{d\delta\phi_i}{dt}=-\frac{1}{m_i\sin\theta_{i0}}\frac{\partial U}{\partial\delta\phi_i},\qquad \frac{1}{\gamma}\frac{d\delta\theta_i}{dt}=\frac{1}{m_i\sin\theta_{i0}}\frac{\partial U}{\partial\delta\phi_i}.\qquad i=3,4 \tag{3}$$

Assuming an $e^{i\omega t}$ time dependence for $\delta\theta_i$ and $\delta\phi_i (i=1,2,3,4)$, the resonance matrix can be solved for its eigenfrequencies.[8] The result is that there are four modes, two modes are AFR modes and the remaining two are nuclear modes. The resonance frequencies are given by[9]

$$\omega_{e\mathrm{I}}^2+\omega_{n\mathrm{I}}^2=\Omega_0^2+\Gamma^2H_0^2\left(1+\frac{H_1}{2H_e}\right)+\omega_0^2+\Gamma^2\alpha mH_1,\qquad \omega_{e\mathrm{I}}^2\omega_{n\mathrm{I}}^2=\omega_0^2\Gamma^2H_0^2\left(1+\frac{H_1}{2H_e}\right), \tag{4}$$

$$\omega_{e\mathrm{II}}+\omega_{n\mathrm{II}}^2=\Omega_0^2+\Gamma^2H_0^2\left(1+\frac{H_1}{2H_e}\right)+\omega_0^2+\Gamma^2H_1(2H_e+\alpha m), \tag{5}$$

$$\omega_{e\mathrm{II}}^2\omega_{n\mathrm{II}}^2=\Gamma^2\omega_0^2\left[H_0^2\left(1+\frac{H_1}{2H_e}\right)+2H_eH_1\right],$$

where $\Omega_0^2=\Gamma^22\lambda\alpha mM$, $H_1=(K_1/M)$, ω_0 is the NMR frequency in the hyperfine field and $H_e=\lambda M$. We shall be concerned with $\omega_{e\mathrm{I}}$ and $\omega_{n\mathrm{I}}$ since the frequency depression of $\omega_{n\mathrm{II}}$ is negligible ($\omega_{e\mathrm{II}}\sim10^{12}$/sec). The term

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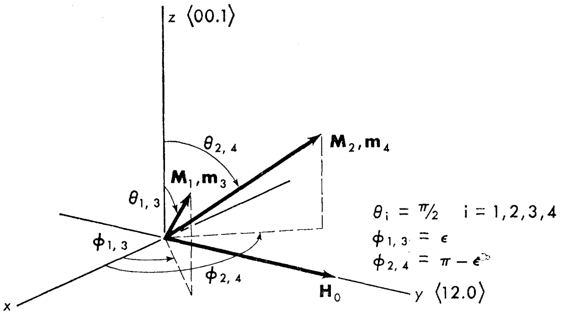

FIG. 2. The polar coordinate system and equilibrium positions for the sublattice magnetizations for CsMnF$_3$.

$\Omega_0^2 = \Gamma^2 2\lambda\alpha mM$ represents the contribution of the hyperfine interaction to the anisotropy energy of the electrons; the effect of this term was first observed in AFR studies in the antiferromagnet KMnF$_3$.[8]

The AFR mode with frequency ω_{eI} is the low-frequency mode given by Lee when the sixfold anisotropy is set to zero. Equation (4) can be rewritten to give

$$\omega_{nI}^2 = \omega_0^2(1 - (\Omega_0^2 + \Gamma^2\alpha m H_1)/(\omega_{eI}^2 - \omega_0^2)). \tag{6}$$

The enhancement factor for resonance absorption is found by introducing the term $-\mathbf{h}e^{i\omega t}\cdot(\mathbf{M}_1+\mathbf{M}_2)$ into Eq. (1) and solving the equations of motion for $\delta\theta_i$ and $\delta\phi_i$ ($i = 1, 2$). The enhancement factor η is given by

$$\eta = (\Gamma^2/\gamma)(\omega_0/\omega_{eI}^2)H_0 \tag{7}$$

for $\mathbf{h}_0$ parallel to the ⟨10.0⟩ axis.

EXPERIMENTAL RESULTS

The NMR frequency is sensitive to an applied dc magnetic field via the field dependence of the AFR frequency (Fig. 3). The method used to detect the nuclear resonance was to measure the change in radio-frequency power reflected from the shorted end of a coaxial line as the magnetic field is swept through the resonance. Field modulation was employed to generate an ac component in the detected voltage, and then standard NMR techniques were used to display the resonance. A 1N21B diode was used as the detecting element; a signal to noise ratio of 50 was not uncommon because of the large enhancement factor for resonance absorption. The single crystal of CsMnF$_3$ was supplied by Dr. R. W. H. Stevenson of the University of Aberdeen. We failed to detect the sixfold in-plane anisotropy that was observed by Lee *et al.*[1]; this result was confirmed by direct AFR experiments. It is possible that the sixfold anisotropy observed in earlier studies was caused by a small contamination of an impurity iron group ion (possibly Fe^{+2}). To estimate the impurity concentration necessary to produce a sixfold anisotropy, we take the spin-orbit coupling to sixth order in perturbation and get $U \cong \lambda(\Delta g)^5$ as the magnitude of the sixfold anisotropy, where λ is the spin-orbit coupling parameter and Δg is the shift in g value of the impurity ion from the spin-only value. If $\lambda \sim 100$ cm^{-1} and $\Delta g = 0.5$, an impurity concentration of 0.04% would produce a 1-Oe sixfold anisotropy.

For applied dc magnetic fields (1000 Oe ~ 7000 Oe) in a ⟨12.0⟩ crystal direction we observed one nuclear resonance. There are two inequivalent sites for the Mn^{2+} ion in CsMnF$_3$. To understand why we have observed only one "frequency-pulled" nuclear resonance, we have solved a four-sublattice antiferromagnet with two different hyperfine interactions for its NMR frequencies. To simplify the model, we have used an orthorhombic single-ion anisotropy energy for the magnetic electrons. The magnetic energy of the nuclear-electron system is given by

$$\begin{aligned} U = {} & \lambda(\mathbf{M}_1+\mathbf{M}_3)\cdot(\mathbf{M}_2+\mathbf{M}_4) \\ & + \sum_{i=1}^{4}(K_1 M_{iz}^2/M_0^2 - K_3 M_{ix}^2/M_0^2) \\ & - \alpha_1\mathbf{m}_5\cdot\mathbf{M}_1 - \alpha_2\mathbf{m}_6\cdot\mathbf{M}_3 - \alpha_1\mathbf{m}_7\cdot\mathbf{M}_2 - \alpha_2\mathbf{m}_8\cdot\mathbf{M}_4. \end{aligned} \tag{8}$$

The single-ion anisotropy K_3 has been introduced to stabilize the system in the xy plane. We find that Eq. (8) has four NMR modes; the nuclear-resonance frequencies for $\omega_e^2 \gg \omega_n^2$ are given by

$$\begin{aligned} & \omega_{n1,3}^2\omega_{n2,4}^2 = \omega_{01}^2\omega_{02}^2[1 - 2\omega_e(\omega_{n1}+\omega_{n2})/\omega_{e1,2}^2], \\ & \omega_{n1,3}^2 + \omega_{n2,4}^2 = \omega_{01}^2(1 - 2\omega_{n1}\omega_e/\omega_{e1,2}^2) \\ & \qquad\qquad + \omega_{02}^2(1 - 2\omega_{n2}\omega_e/\omega_{e1,2}^2), \end{aligned} \tag{9}$$

where $\omega_{01,2} = \gamma\alpha_{1,2}|M|$, $\omega_{n1,2} = \Gamma\alpha_{1,2}|m_{1,2}|$, $\omega_e = \Gamma\lambda|M|$, and $\omega_{e1,2}$ are the resonance frequencies of the two low-lying AFR modes. The form of the equations for the nuclear-resonance frequencies given by Eq. (9) is quite

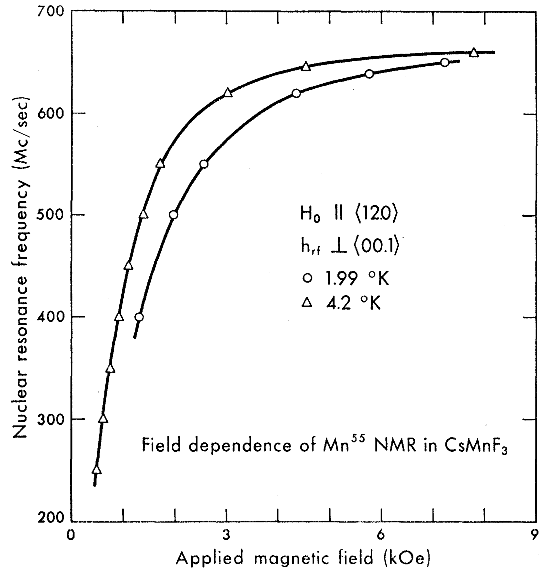

FIG. 3. The field dependence of the Mn^{55} NMR frequency for H_0 parallel to the ⟨12.0⟩ axis.

general; their validity is not limited to magnetic systems with orthorhombic symmetry. In Fig. 4 we have plotted the two solutions to Eq. (9) for $\omega_{01}=0.95\omega_{02}$ as a function of the pulling parameter $2\omega_e\omega_{n2}/\omega_{e1}^2$. Of the two solutions, then, only one NMR frequency is "pulled" to any great extent. It is interesting to note, however, that the nuclear mode with the resonance frequency ω_{n2} is pulled for $2\omega_e\omega_{n2}/\omega_{e1}^2\sim 0$ and then saturates very rapidly as the pulling parameter increases. It is possible that the field shifts for AFR observed by Lee *et al.*[1] in the double-resonance experiments for rf frequencies greater than 668 Mc/sec are the result of driving the nuclear system in this high-frequency mode. In view of the discussion given above, it is not very surprising that we have observed only one nuclear resonance in $CsMnF_3$, since the NMR mode with the resonance frequency given by Eq. (5) would have no appreciable "frequency pulling" ($\omega_{eII}\sim 10^{12}$/sec). We identify mode I as the electron mode that has been used to excite the nuclear resonance in our experiment. To verify the quadratic dependence of the AFR frequency on applied field, we plot $(1-\omega_n^2/\omega_0^2)^{-1}$ versus H_0^2; the result is shown in Fig. 5. The agreement is very good; the absence of a term linear in applied field indicates that canting is not important in this material.

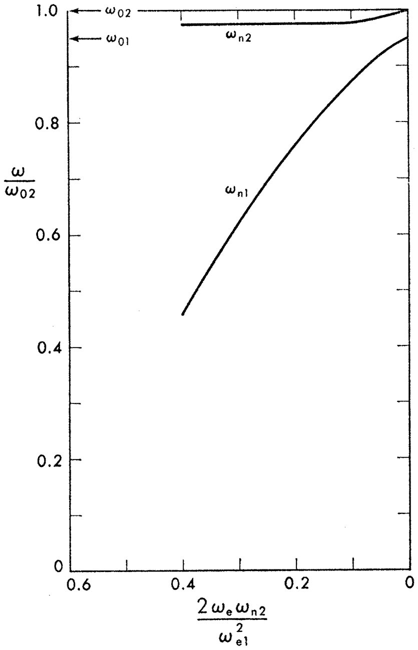

FIG. 4. A plot of the two solutions of Eq. (9) for $\omega_{01}=0.95\omega_{02}$ versus the pulling parameter $2\omega_e\omega_{n2}/\omega_{e1}^2$.

For temperatures in the liquid-helium temperature range, the nuclear sublattice magnetization should have the characteristic T^{-1} dependence of a paramagnet; from Eq. (6) we plot $(\omega_n/2\pi)^2$ versus T^{-1} for a constant AFR frequency. The result is given in Fig. 6.

We have also performed direct AFR experiments. We find that the field for resonance predicted by Eqs. (5) is approximately in 2% error. To account for the error in resonance field, we have included demagnetization and relaxation effects (Landau-Lifshitz[10] relaxation was included in the equation of motion for the electronic magnetization); even with these corrections we have been unable to correct the error. It is possible that anisotropic hyperfine coupling and quadrupolar effects in the nuclear spin system (the Mn^{55} nucleus has a spin of $\frac{5}{2}$) could account for the discrepancy.

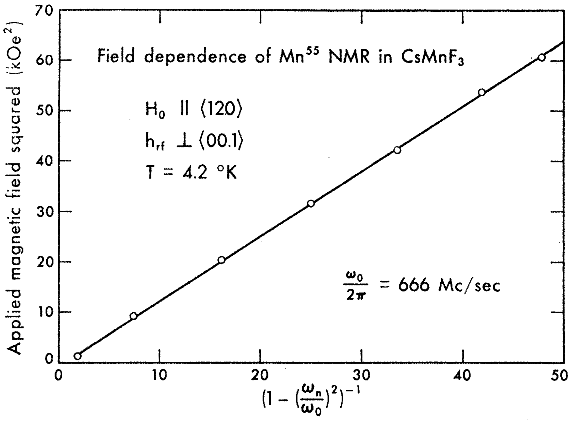

FIG. 5. A plot of the quardatic field dependence of the AFR frequency for $CsMnF_3$.

DISCUSSION

The results of the direct NMR experiments on $CsMnF_3$ are in good agreement with the two-sublattice model proposed by Lee. We have not included an anisotropy energy to stabilize the spins in the (00.1) plane; as a consequence, $\omega_{nI}\rightarrow 0$ as $H_0\rightarrow 0$ [see Eqs. (5)]. NMR experiments have been extended to lower

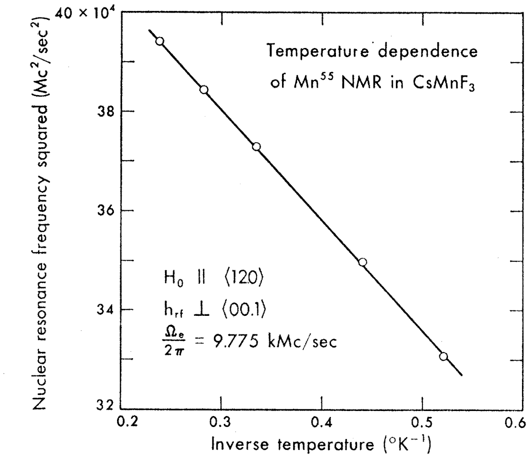

FIG. 6. The temperature dependence of the nuclear-resonance frequency for constant AFR frequency.

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fields ($H_0=150$ Oe) in an attempt to determine the zero-field nuclear-resonance frequency. The result is that if we extrapolate from $H_0=150$ Oe we find that $\omega_n(H_0=0)/2\pi \sim 40$ Mc/sec. To account for this zero-field NMR frequency, an in-plane anisotropy of order 10^{-2} Oe would be sufficient. The very low in-plane anisotropy energy for the magnetic electrons in $CsMnF_3$ results in a high degree of "frequency pulling" for the NMR frequency; $CsMnF_3$ is a most striking example of the importance of cooperative effects in tightly coupled nuclear-electron systems.

We have used $H_e=3.1\times10^5$ Oe and $\omega_0/2\pi=666$ Mc/sec to obtain the theoretical fit to the experimental results. If volume corrections for the F^- octahedra surrounding a Mn^{2+} ion are made, Ogawa's[11] paramagnetic resonance studies would give $\omega_0/2\pi=687\pm7$ Mc/sec as the value for the average hyperfine field frequency; this would suggest a $3.0\pm1.0\%$ zero-point spin-wave reduction in $\langle S\rangle$ for $CsMnF_3$. The linked-cluster expansion calculated by Davis[12] predicts a 4.36% reduction in $\langle S\rangle$.

The excitation of the nuclear resonance by the applied rf magnetic field is via an indirect mechanism. The resonance is excited by a rocking of the electronic sublattice magnetization[13] at the driving rf frequency. From Eq. (7), if $H_0=3000$ Oe and $T=4.2$°K one has $\eta\cong150$, which gives a signal to noise enhancement of $\sim2\times10^4$.

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Magnetic Moments and Unpaired-Electron Densities in $CoPt_3$

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A polarized-neutron investigation of the ferromagnetic alloy $CoPt_3$ in various degrees of chemical order is presented. The magnetic moments of the two components have been determined; that of the cobalt is $1.64\pm0.04\,\mu_B$, and that of the platinum $0.26\pm0.02\,\mu_B$ in the fully ordered material. The experimental form factors of platinum and cobalt were measured and it is shown that they are in fair agreement with recent theoretical calculations. A Fourier inversion of the data was also carried out to show the t_{2g} character of the cobalt d electrons of this alloy.

I. INTRODUCTION

SEVERAL theoretical and experimental investigations have been recently carried out on the microscopic magnetic properties of $3d$ transition elements and their alloys. However, little is known about other elements where the incomplete inner shells of electrons are the $4d$ or $5d$. They do not exhibit any ferromagnetism in the pure metallic state but seem capable of ferromagnetic interaction when alloyed with elements of the iron transition group. Magnetization measurements of such alloys at different concentrations[1] lead to the hypothesis that both $4d$ and $5d$ atoms can interact magnetically, and this hypothesis has been recently confirmed by neutron-diffraction studies for some $4d$ elements, namely Pd,[2,3] Rh,[4] and Zr.[5] However, the magnetization results are difficult to interpret and the models proposed to explain the measurements were often admitted to be inadequate.[1]

Among the $5d$ elements Pt has attracted the attention of many investigators. Bulk magnetization has been measured for several ferromagnetic alloys with $3d$ elements and the neutron diffraction technique has been used for Co-Pt,[6] Mn-Pt, and Cr-Pt[7] systems. The presence of a magnetic moment on the Pt atom has been

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