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COMMENTS AND ADDENDA

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Local Antiferromagnetic Ordering in Ferromagnetic $MnPt_3$ Alloys near the Stoichiometric Composition

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The magnetic-moment density distribution in two alloys near the stoichiometric $MnPt_3$ alloy composition has been measured by means of the polarized-neutron technique. It has been found that in the perfectly ordered lattice Mn and Pt atoms are ferromagnetically aligned, while in the presence of disorder the Mn atoms which happen to occupy the Pt sites give a negative contribution to the magnetization. The spherically averaged distribution for Mn atoms is independent of whether the atom is on a Mn or Pt site. However, Mn atoms on Mn sites are spherically symmetric, while Mn atoms on Pt sites have aspherical distributions.

An extensive study of the magnetization distribution at microscopic level in ferromagnetic alloys of Pt with 3*d* elements is in progress in our laboratory by means of polarized-neutron diffraction.[1-3] It was recently found that the stoichiometric ferromagnetic alloy $MnPt_3$ with incomplete long-range chemical order exhibits a negative magnetization at the center of the sites of the platinum atoms.[3] (The alloy has the Cu_3Au superlattice structure.) Antiferromagnetic coupling of the Mn atoms which happen to be on the Pt sites was considered to be the origin of the negative magnetization. Clearly this hypothesis had to be confirmed by other experimental evidence since it would be of some interest to prove the existence of isolated antiferromagnetically coupled atoms in a ferromagnetic metallic matrix. Therefore we have determined the distribution of magnetization in an alloy of higher manganese content in order to vary the relative number of atoms on each site thereby obtaining an independent test of the above hypothesis.

A single crystal of composition $Mn_{0.282}Pt_{0.718}$ was obtained[4] and the long-range degree of order S was measured to be $S = 0.974 \pm 0.010$ (only statistical error), which is somewhat higher than the maximum value compatible with this composition, 0.956. The alloy was found to be ferromagnetic with a magnetic moment at 77 °K of $(3.78 \pm 0.05)\mu_B$ per unit cell. The percentage occupancy of the atomic sites in this case and in the previous one[3] is given in Table I.

All of the reflections have been measured at liquid-nitrogen temperature out to $(\sin\vartheta)/\lambda = 0.769$ Å^{-1} and the results are shown in Fig. 1 for both compositions. One can observe that in both cases the magnetic structure factors belong to two different curves: one for the superlattice and one for the fundamental reflections, which means that the Pt sites have a nonzero magnetic moment. Moreover, the behavior of the two curves is different in the two cases since in $Mn_{28}Pt_{72}$ the fundamental reflections are closer to the superlattice ones at small values of $(\sin\vartheta)/\lambda$ than they were in $MnPt_3$ and are farther apart at high values of $(\sin\vartheta)/\lambda$. Thus the magnetic moment of the Pt site is strongly affected by the Mn atoms, which are more abundant on the Pt sites for the case of the $Mn_{28}Pt_{72}$ alloy.

The data were analyzed under the hypothesis that, at least for these small deviations from perfectly ordered stoichiometric $MnPt_3$, the contributions of Mn and Pt atoms which are on unordered sites are simply proportional to their occupation probability, i.e., that there are no effects dependent on S^2 or higher powers of S. Therefore we define the magnetic structure factors as given by

$$F_f(\vec{\tau}) = \mu_{\mathrm{Mn}} f_{\mathrm{Mn}}(\vec{\tau}) p_{1\,\mathrm{Mn}} + \mu_{D1} f_{D1}(\vec{\tau}) p_{1\,\mathrm{Pt}} + 3\left[\mu_{\mathrm{Pt}} f_{\mathrm{Pt}}(\vec{\tau}) p_{2\,\mathrm{Pt}} + \mu_{D2} f_{D2}(\vec{\tau}) p_{2\,\mathrm{Mn}}\right] \quad (1)$$

for fundamental reflections and

$$F_s(\vec{\tau}) = \mu_{\mathrm{Mn}} f_{\mathrm{Mn}}(\vec{\tau}) p_{\mathrm{Mn}} + \mu_{D1} f_{D1}(\vec{\tau}) p_{1\,\mathrm{Pt}} + - \left[\mu_{\mathrm{Pt}} f_{\mathrm{Pt}}(\vec{\tau}) p_{2\,\mathrm{Pt}} + \mu_{D2} f_{D2}(\vec{\tau}) p_{2\mathrm{Mn}}\right] \quad (2)$$

for superlattice reflections; $\vec{\tau}$ is the reciprocal-lattice vector of the magnetic reflections; μ_{Mn} and μ_{Pt} are the magnetic moments of Mn and Pt, respectively, in the undisturbed conditions, while f_{Mn} and f_{Pt} are their form factors; μ_{D1} is the magnetic moment of the disturbance due to the presence of Pt atoms on the Mn sites while μ_{D2} is that due to the presence of Mn atoms on the Pt sites; f_{D1} and f_{D2} are the form factors of these disturbances; p_{iA} are the occupation probabilities of the site i by the atom A, $i=1$ being the site of Mn atoms and $i=2$ that of Pt atoms. Equations (1) and (2) are applied to both compositions. Since from the Fourier inversion of the data there was no evidence of an appreciable constant (negative or positive) magnetic moment such as was found in other ferromagnetic metals and alloys,[5-8] it was neglected in the present scheme. To solve Eqs. (1) and (2) where there are four unknown magnetic moments plus four unknown form factors which are dependent on the value of $\vec{\tau}$, we first obtained the values of the magnetic moments of each atomic site in both materials by integration of the magnetization, which is the Fourier inversion of the magnetic structure factors over spheres centered on the atomic sites. This can be done analytically since the magnetic moment within any spherical region is given by

$$\mu_i = \frac{4\pi R^3}{V_c} \sum_{\vec{\tau}} F(\vec{\tau}) e^{2\pi i \vec{\tau}\cdot\vec{r}_i} \left(-\frac{\cos 2\pi\tau R}{(2\pi\tau R)^2} + \frac{\sin 2\pi\tau R}{(2\pi\tau R)^3} \right), \quad (3)$$

where R is the radius of the sphere, $\vec{r}_i$ is the position of its center with respect to the origin of the unit cell, and V_c is the volume of the unit cell. It can be seen that the series is rapidly converging for increasing τ due to the power of τ in the denominators.

This equation can be used to calculate the magnetic moments when there is no appreciable overlap of the electron distribution; it is a different approach from that proposed by Moon,[9] who gives a formula for obtaining the individual magnetic moments without using the value of the total magnetic moment of the cell. He has to introduce the hypothesis that the magnetic atoms are in a "sea" of constant magnetic-moment density. In our case we have no experimental evidence for such a constant magnetization in this material.[3]

In order to check the validity of Eq. (3) in our case we tested the dependence of the calculated magnetic moments with R, the radius of the integration sphere. It was found possible to find values of R both for the Mn and Pt sites such that the magnetic moments could be determined without ambiguity; for instance, in the case of the $\mathrm{MnPt_3}$ alloy the Pt-site magnetic moment was found to vary only 2% for a 10% variation of R about the value given by one-half the Mn-Pt interatomic distance.

A smaller variation was found for the Mn sites, as expected, since the $5d$ magnetic electrons of Pt are much more spread than the $3d$ electrons of Mn.

The question of whether the integration volumes contained all of the magnetic electrons was investigated by means of a test calculation; i.e., by using a theoretical $5d$ form factor for $\mathrm{Pt^{2+}}$, given by Cromer and Waber,[10] we generated a set of magnetic structure factors for a hypothetical ferromagnetic pure-Pt metal having the same structure and lattice parameter as $\mathrm{MnPt_3}$. These magnetic structure factors, which extended to the same range of $(\sin\theta)/\lambda$ as the measured $\mathrm{MnPt_3}$ values, were used to calculate the percentage of Pt moment obtained with Eq. (3) as a function of R. It was

TABLE I. Occupation probability of the Pt and Mn sites for the alloy of the present work and the one considered in Ref. 3 (the degree of order has been found in this last material to be 0.906 ± 0.010, which is an improved value because of more extensive measurements over that reported earlier, 0.92 ± 0.02).

Alloy	S Degree of order	$p_{1\,\mathrm{Mn}}$ Mn atoms on Mn sites	$p_{2\,\mathrm{Mn}}$ Mn atoms on Pt sites	$p_{2\,\mathrm{Pt}}$ Pt atoms on Pt sites	$p_{1\,\mathrm{Pt}}$ Pt atoms on Mn sites
$\mathrm{MnPt_3}$	0.906 ± 0.010	0.928 ± 0.010	0.022 ± 0.005	0.978 ± 0.010	0.072 ± 0.005
$\mathrm{Mn_{28}Pt_{72}}$	0.956 ± 0.010	$1\begin{cases}+0\\-0.010\end{cases}$	0.043 ± 0.005	0.956 ± 0.010	$0\begin{cases}+0.005\\-0.000\end{cases}$

found that for R equal to one-half the Mn-Pt interatomic distance, 95% of the moment was inside the integration sphere; a lower value of R was needed to obtain 100% of the Mn moment. Therefore Eq. (3) was used to determine the magnetic moments of the sites.

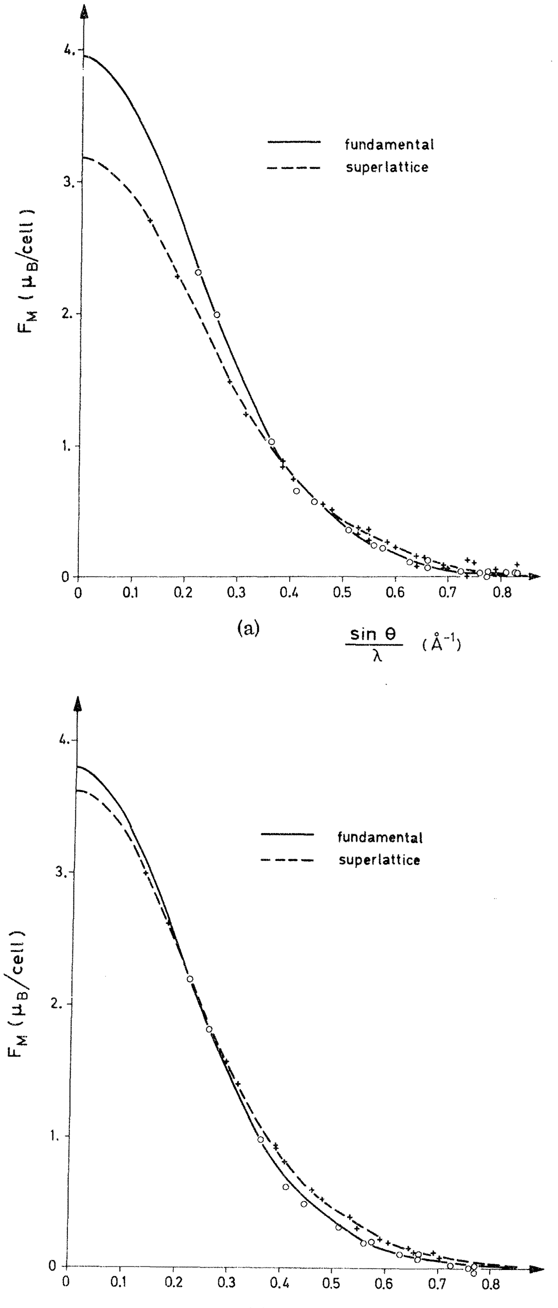


FIG. 1. Magnetic structure factors in Bohr magnetons per unit cell at liquid-nitrogen temperature for $MnPt_3$ (a) and $Mn_{28}Pt_{72}$ (b). The lines represent the spherical structure factors which have been calculated as described in the text. The fundamental reflections are represented by the circles; the superlattice ones by the crosses.

From the magnetic moments of the sites for both compositions we can now calculate the individual magnetic moments μ_{Mn}, μ_{Pt}, μ_{D1}, and μ_{D2} since we have $\mu_1=\mu_{\mathrm{Mn}}p_{1\,\mathrm{Mn}}+\mu_{D1}p_{1\,\mathrm{Pt}}$ and $\mu_2=\mu_{\mathrm{Pt}}p_{2\,\mathrm{Pt}}+\mu_{D2}p_{2\,\mathrm{Mn}}$ for each composition. We found at 77 °K $\mu_{\mathrm{Mn}}=3.66\pm0.04$, $\mu_{\mathrm{Pt}}=0.35\pm0.02$, $\mu_{D1}=-0.4\pm1.1$, and $\mu_{D2}=6.7\pm2.3$, all values given in Bohr magnetons.

Equations (1) and (2) cannot be solved to obtain the form factors since fundamental and superlattice reflections are measured at different $\vec{\tau}$ vectors. However, it is possible to calculate from the experimental magnetic structure factors the form factors of the sites as continuous functions of $(\sin\vartheta)/\lambda$ for any direction and from these solve for the form factors of the atoms on each site. Actually, one finds that the spherical form factors of the sites are related to the experimental magnetic structure factors $F(\vec{\tau})$ by means of the following expression, which is obtained by taking the spherically averaged Fourier inversion of the magnetization distribution inside a sphere of radius R and centered on the site $\vec{r}_i$:

$$f_i(K)=\frac{2\pi R^3}{V_c}\,\frac{1}{KR}\sum_{\vec{\tau}}\frac{F(\vec{\tau})}{\mu_i}\,e^{2\pi i\vec{\tau}\cdot\vec{r}_i}\,\frac{1}{2\pi\tau R}\times\left(\frac{\sin(K-2\pi\tau)R}{(K-2\pi\tau)R}-\frac{\sin(K+2\pi\tau)R}{(K+2\pi\tau)R}\right), \qquad (4)$$

where $K=4\pi(\sin\vartheta)/\lambda$ is a continuous variable; one can note that

$$\lim_{K\to0}f_i(K)=1 \quad .$$

This method of obtaining spherically symmetric form factors from the measured magnetic structure factors has been described by Moon.[9] By then using the expressions which relate the site form factors to the individual form factors, i.e.,

$$\mu_1f_1(K)=\mu_{\mathrm{Mn}}p_{1\,\mathrm{Mn}}f_{\mathrm{Mn}}(K)+\mu_{D1}p_{1\,\mathrm{Pt}}f_{D1}(K)\ , \qquad (5)$$

$$\mu_2f_2(K)=\mu_{\mathrm{Pt}}p_{2\mathrm{Pt}}f_{\mathrm{Pt}}(K)+\mu_{D2}p_{2\,\mathrm{Mn}}f_{D2}(K)\ , \qquad (6)$$

we can obtain the individual spherical form factors. However the form factor of the disturbance on the Mn site was found to be not significant because of the very large error in the magnetic moment of the disturbance. The form factors of the Mn atom and that of the disturbance on Pt sites are compared in Fig. 2 where it appears that they are identical within experimental errors which are about 30% for the disturbance form factor. This suggests that the antiferromagnetic disturbance on the Pt sites is due to antiferromagnetically coupled Mn atoms of magnetic moment $\mu_{D2}=(-6.7\pm3)\mu_B$.

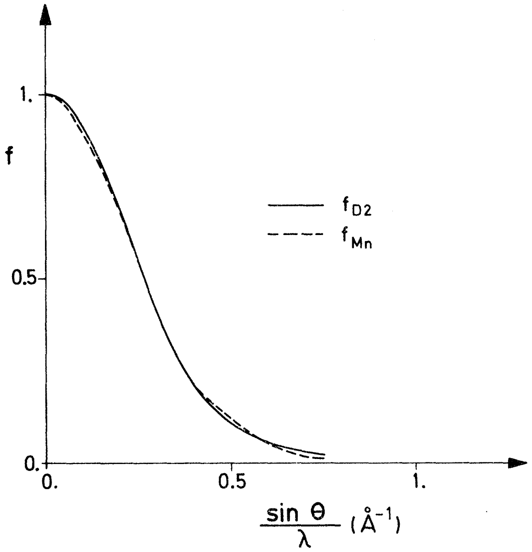


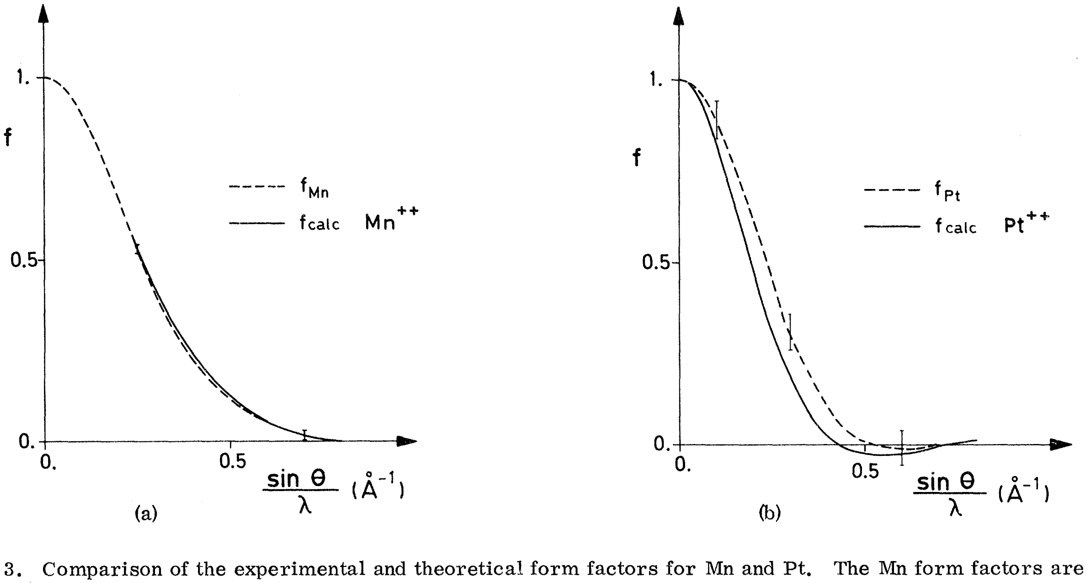
FIG. 2. Comparison of the magnetic form factor for Mn atoms on their sites and for the disturbance due to antiferromagnetically coupled Mn atoms on the Pt sites.

The magnetic form factors for Mn and Pt are then compared with theoretical free-atom calculations in Fig. 3. The Mn-atom form factor is identical within experimental errors, which are never higher than 0.01 units, with the free-ion spin-only Mn^{2+}-form-factor calculation of Watson and Freeman.[11] The Pt-atom form factor is compared with the relativistic calculations of Cromer and Waber[10] for the 5*d* shell of free Pt^{2+} ions. In the case of Pt there appears to be a difference between calculated and experimental form factors which might be due to the presence of an orbital contribution to the magnetic moment of the Pt atom, which should be in an incomplete 5*d* shell state, contrary to the case of Mn^{2+} ions, which are expected to have an almost half-filled 3*d* shell.

The possibility of disturbances due to the misplaced Mn atoms on the magnetic moments of Pt atoms in the same cell or in neighboring ones could not be excluded; however, the fact that the form factor of the disturbance is very close to that of the Mn atoms should be an indication that most of the disturbance is solely confined to the misplaced Mn atoms.

The spherical form factors of Mn and Pt and disturbances have been used to calculate the smooth structure-factor curves shown in Fig. 1. As far as the aspherical contribution to the form factor, one can observe from Fig. 1 that the asphericities which appear in the case of the $MnPt_3$ alloy are considerably reduced in the other alloy. Conceivably this may be ascribed to a competing asphericity of the Mn atoms on the Pt sites.

From the Fourier inversion of the data it appears that the asphericity is confined to the Pt sites while the Mn sites appear to be completely spherical. The problem of obtaining the populations for both Pt and Mn on the Pt sites of the four sublevels[3] which originate from the splitting of any *d* level in the tetragonal crystalline field of the Pt sites has proved to lead to inconclusive results because of the limited amount of data and the relatively large experimental errors. However, it was possible to conclude that Mn on the Pt sites has about the



(a) (b)

FIG. 3. Comparison of the experimental and theoretical form factors for Mn and Pt. The Mn form factors are compared with the free-atom calculations of Watson and Freeman for the Mn^{++} state (Ref. 10). The Pt form factor is compared with the relativistic free-atom calculation of Cromer and Waber for the Pt^{++} configuration (Ref. 11).

same asphericity as Pt and that both have a predominant symmetry of the type A_1 and B_2, which are the two sublevels in which the e_g cubic level is split by the tetragonal field.

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Fluctuation Spectra in Interacting Spin Systems

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A close parallel is demonstrated between recent room-temperature studies of Gd 4*f* spin-exchange fluctuations via ^{31}P NMR relaxation rates by Myers and Narath and earlier work on the dipolar fluctuations in CaF_2 via ^{43}Ca-^{19}F cross-relaxation rates by McArthur, Hahn, and Walstedt. Both spectra vary quasiexponentially with frequency, in conflict with the diffusion model of spin correlation developed by Gulley, Hone, Scalapino, and Silbernagel. The theoretical treatment of spin correlation by Blume and Hubbard is shown to exhibit, at low frequencies, the exponential character in the spectral density found in these experiments. The "diffusion tail" predicted by many theories of spin correlations is thus found in three-dimensional systems to play a relatively minor role in the power spectrum.

I. INTRODUCTION

Recently a letter was published by Myers and Narath[1] reporting experimental measurements of the high-temperature exchange-fluctuation spectrum in GdP. This study was carried out by measuring ^{31}P nuclear relaxation rates which reflect the fluctuations among the Ruderman-Kittel-Yosida (RKY) exchange-coupled Gd 4*f* moments. The spectrum obtained was interpreted with the diffusion model of spin-spin correlation functions developed by Gulley *et al.*[2]

In this note we highlight an alternate viewpoint on the Myers-Narath results which is suggested by earlier work by McArthur, Hahn, and Walstedt[3] on rotating-frame nuclear-spin cross-relaxation times in CaF_2. We demonstrate a close parallel between the experiments of Refs. 1 and 3 and note an empirical similarity in the outcomes. Second, we argue that the diffusion-model theory[2] is in basic conflict with the results from both Refs. 1 and 3 as well as with the recent theoretical work of Blume and Hubbard (BH).[4] Explicit estimates are made of the importance of diffusion effects in these phenomena.

II. CROSS-RELAXATION TIMES AND SPIN-SPIN AUTOCORRELATION FUNCTIONS

In both the GdP: ^{31}P NMR studies[1] and the earlier rotating-frame nuclear-double-resonance work on CaF_2: ^{43}Ca one is concerned with weak cross coupling between one spin species (No. 1) and the "bath" of rapid fluctuations belonging to a second (No. 2). If the cross-relaxation time is τ_{12} and the correlation time of the fluctuations is τ_c, then by "weak" coupling we mean $\tau_{12} \gg \tau_c$. τ_{12} is then given by the equation[3]

$$\frac{1}{\tau_{12}} = \Omega^2 \int_{-\infty}^{\infty} dt\, e^{i\omega t} \left(\frac{\mathrm{Tr}(H_{12} e^{iH_{22}t} H_{12} e^{-iH_{22}t})}{\mathrm{Tr}\, H_{12}^2} \right), \tag{1}$$

since the fluctuation baths are essentially at infinite temperature. In Eq. (1) H_{12} and H_{22} are the