Neutron Measurement of Magnetization Density in Palladium*

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The magnetization density induced in palladium by an applied magnetic field was measured by polarized neutron diffraction. The measurements were taken with the sample at 4.2 K in an applied field of 57.2 kOe and include the innermost eleven Bragg reflections. The observed density is contracted by about 15% relative to that calculated for Pd^{+2} by the Hartree-Fock method, and shows an asphericity similar to that of isoelectronic Ni.

Magnetic-form-factor studies[1-3] show that the spin densities of the 3*d* transition-metal ferromagnets are appreciably contracted relative to those calculated for Hartree-Fock free atoms. It has been suggested[4,5] that this contraction is associated with the radial character of the antibonding wave functions near the top of the *d* band in the metals.[6,7] However, the experimental spin densities for ferromagnetic metals are not in good agreement with those obtained from band-structure calculations[8-11]; it is rather puzzling that their shape is instead closely approximated by those of the Hartree-Fock free ions in the +2 ionization state.[12] Some of the computational difficulties associated with the ferromagnetic state are avoided in the paramagnetic state which therefore affords a more direct comparison between theory and experiment. We have chosen to measure the magnetic form factor and the corresponding density associated with the field-induced moment of paramagnetic palladium, an element that exhibits very high susceptibility,[13] with nearly spin-only character.[14] We find that the magnetization density contraction is more pronounced for Pd than for the 3*d* ferromagnets.

The experimental method is the same as that used for ferromagnetic systems and consists of taking the intensity ratio at the Bragg positions (*hkl*) for neutrons with spins parallel and antiparallel to the sample magnetization. With the proper experimental geometry, this ratio is

$$R_{hkl} = (b + p_{hkl})^2/(b - p_{hkl}), \quad (1)$$

in which b and p are the nuclear and magnetic scattering amplitudes. The nuclear amplitude is a known constant ($b = 0.591 \times 10^{-12}$ cm),[15] while p is proportional to the induced moment per atom and to the magnetic form factor appropriate to the *hkl* reflection.

The samples were rod-shaped single crystals, 1 mm in diameter and 15 mm long, with a [110] axis parallel to the rod. Magnetization measurements on the two samples for which neutron data were collected show that one is very pure[13] while the other contains about 44 ppm of a superparamagnetic impurity. The superparamagnetic cluster moment is about $13\mu_B$ per impurity which is characteristic[16] of Fe impurities in Pd.

The neutron measurements were made at the high-flux isotope reactor at Oak Ridge National Laboratory. Extinction checks were made by measuring R_{111} as a function of neutron wavelength. The "as-grown" crystals[17] showed appreciable extinction (30% at 1 Å) and a reflectivity corresponding to a mosaic spread of ~2 min. After a gentle rolling and the consequent deformation to a mosaic spread of ~16 min, the crystals showed no change in R_{111} from 0.768- to 1.41-Å neutron wavelength and thus appear to be free of extinction.

Intensity ratios were taken for the eleven innermost reflections at 4.2 K in an applied field of 57.2 kOe. Under these conditions, the total induced moment is $7.5 \times 10^{-3}\mu_B$ and $8.0 \times 10^{-3}\mu_B$ per atom for the two samples. This moment contains three components: the 4*d* moment, the diamagnetic moment, and the localized-impurity moment. The observed magnetic amplitudes were corrected for the diamagnetic[18] and local-impurity contributions by assuming the diamagnetic susceptibility of Ag^+ and that the superparamagnetic clusters are caused by Fe atoms with a localized moment of $3\mu_B$ per Fe. These corrections are small (<3%) and readily calculable.

TABLE I. Comparison of the observed and calculated form factors for paramagnetic Pd.

hkl	$\sin\theta/\lambda$	f_{obs}	f_{calc}[a]
111	0.223	0.536±0.015	0.553
200	0.258	0.433±0.015	0.407
220	0.364	0.178±0.015	0.172
311	0.427	0.035±0.018	0.053
222	0.446	0.070±0.018	0.090
400	0.515	−0.077±0.015	−0.071
331	0.561	0.006±0.018	0.013
420	0.576	−0.045±0.025	−0.030
422	0.631	0.035±0.015	0.001
333	0.669	0.020±0.015	0.030
511	0.669	−0.043±0.015	−0.059

[a]Calculated from Eq. (2) with Hartree-Fock Pd^{+2} form factors and with $\alpha=0.15$ and $\gamma=0.15$.

The corrected amplitudes for the two samples differ only insofar as the 4*d* moments differ and yield the same form factor within experimental error. The average form-factor values are given in Table I.

We first compare the data with an atomic calculation using the same model[1-3] that successfully describes the moment densities of the ferromagnetic transition metals. In this model, free-atom *d*-electron densities are centered at the atomic sites and these are superimposed on a uniform background that can be either positive or negative. The model also allows for an orbital moment and an aspherical *d*-electron distribution. The form factor is then written as

$$f(K)=(2/g)(1+\alpha)[\langle j_0\rangle+(\tfrac{5}{2}\gamma-1)A_{hkl}\langle j_4\rangle]+[(g-2)/g]f_{orb}-(2/g)\alpha\delta(K). \quad (2)$$

The *g* factor, which determines the fraction of the atomic moment associated with unpaired spins, was taken from magnetomechanical measurements[14] to be 2.20. Some question could be raised on the applicability of the gyromagnetic ratio thus obtained from measurements at room temperature. No paramagnetic resonance has been detected in pure palladium; in impure samples (3*d* solute atoms) the resonance experiments give extrapolated values[19] of *g* ranging from 2.1 to 2.5, depending upon the solute. However, it is convenient to fix the value of *g* for the arguments to follow, that do not change by varying *g* in a reasonable region.

The $\langle j_0\rangle$, $\langle j_4\rangle$, and f_{orb} functions were taken from a restricted Hartree-Fock calculation[20] for Pd^{+2}. A_{hkl} is simply a geometrical factor.[21] The two parameters are then α, the fraction of the spin moment appearing as a uniform negative polarization, and γ, the fractional population of the E_g crystal-field sublevels. A least-squares fit of this expression to the observed data yields the parameters $\alpha=0.15\pm0.03$ and $\gamma=0.15\pm0.04$. The corresponding form-factor values are listed in the last column of Table I and are in good agreement with the data. The parameters are nearly the same as those obtained[3] for isoelectronic Ni ($\alpha=\gamma=0.19$) and correspond to a distinctly aspherical density function ($\gamma=40\%$ for a spherical distribution) with a localized moment of $8.8\times10^{-3}\mu_B$ per atom and a uniform polarization of $-1.1\times10^{-3}\mu_B$ per atomic volume. However, we must recognize that α, and therefore the local and nonlocal moment values, is dependent on the form-factor assumption. We have fitted to the Pd^{+2} form factors because of the previous observations on the 3*d* transition-metal ferromagnets. Since this same behavior does not necessarily apply to palladium, we must question the physical significance of α. The γ parameter is, however, relatively insensitive to the form-factor assumption.

The α parameter was checked by direct Fourier transformation of the form-factor data. The resulting moment density is perhaps best illustrated by the point-density map shown in Fig. 1. This map, not too dissimilar from that obtained for a $Fe_{0.013}Pd_{0.987}$ alloy,[22] exhibits large positive-density regions centered at the atomic positions and these have a pronounced asphericity in ac-

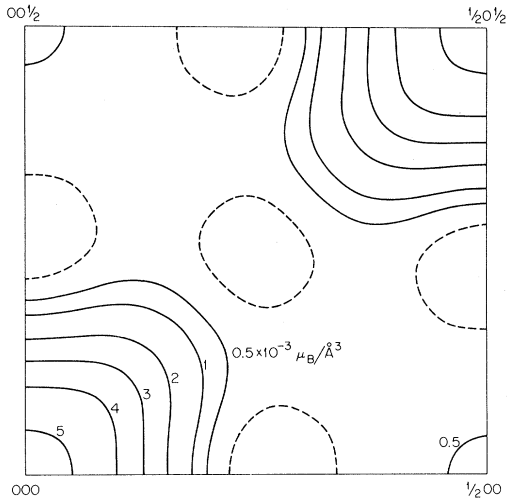

FIG. 1. Moment density in a (100) plane. The dashed lines are zero-density contours.

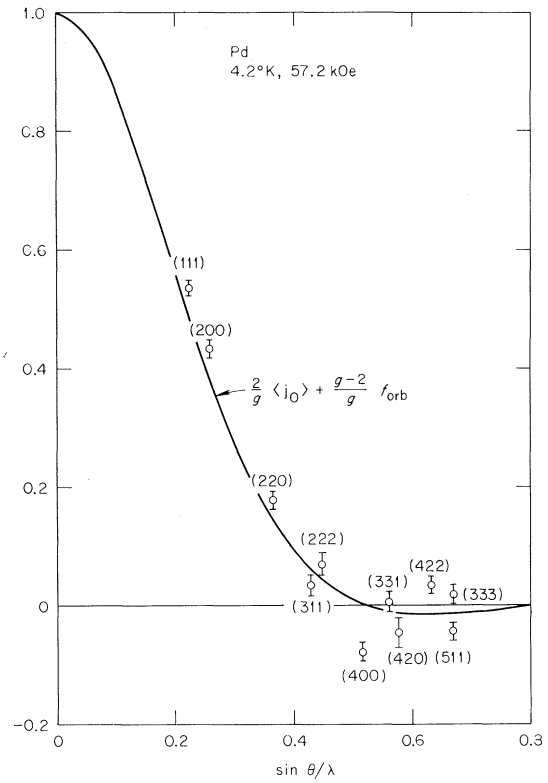

FIG. 2. Experimental form factor of palladium. The continuous line represents the spherically averaged Hartree-Fock form factor of Pd^{2+}.

cordance with the low γ parameter obtained from the free-atom fitting procedure. The low-density features, i.e., the negative-density regions inside the dashed contours and the small positive regions at $\frac{1}{2}00$ and $00\frac{1}{2}$, are questionable because the Fourier sums do not converge well enough to establish their existence. This convergence problem can be avoided to a large extent by averaging the density over some volume element.[23] We have used this technique to obtain better values for the moment density in the low-density regions and obtain good convergence with an averaging sphere of radius 0.5 Å or 13% of the edge of the cell. With this forced convergence, the interatomic moment density varies from $(0.5 \pm 0.6) \times 10^{-3} \mu_B$ per atomic volume at $\frac{4}{10}0\frac{1}{10}$ to $(-0.3 \pm 0.6) \times 10^{-3} \mu_B$ per atomic volume at $\frac{1}{4}0\frac{1}{4}$. Thus, the Fourier analysis shows no appreciable negative polarization in the interatomic region and therefore that the local moment is the same as the $4d$ magnetization. We conclude that the α parameter from the free-atom fit, which requires an interatomic density of $-1.1 \times 10^{-3} \mu_B$ per atomic volume, is nonphysical and that the localized moment density is contracted by about 15% relative to the Hartree-Fock Pd^{+2} density functions that are already contracted by an equal amount relative to the free atom. In Fig. 2 the nonscaled ($\alpha = 0$), spherically averaged ($\gamma = 0$), Hartree-Fock Pd^{2+} form factor is compared with the experimental points, that for the three innermost reflections, most sensitive to the radial distribution, are definitely higher than the expectations. The question of whether the associated contraction of the wave functions can be explained as a solid-state effect is treated in the following Letter.[24]

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Theoretical Determination of the Induced Magnetization Density and Form Factor of Palladium*

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Induced magnetization densities determined from an *ab initio* augmented-plane-wave wave-function study of Pd metal including local density-of-states effects on the Fermi surface were found to yield a neutron magnetic form factor in excellent agreement with the recent experiments of Cable *et al.* A remarkable feature of these solid-state spin densities is their spatial localization which is greater than even the very contracted Hartree-Fock density of the free Pd^{2+} ion.

The present understanding of the electronic structure and properties of the transition metals has come from a variety of experiments yielding macroscopic information or microscopic information which have been related directly to the electronic energy-band structure. By contrast, there are few experiments which yield direct information about the nature of the *wave functions* in these metals. One outstanding exception is the use of neutron magnetic-scattering experiments to yield, via the form factor, the Fourier transform of the magnetization density in the magnetically ordered metals. While theory has been successful, in most cases, in yielding an adequate account of the energy-dependent properties, it has had distinctly poorer success in explaining observed form factors because of the greater theoretical (and computational) problem associated with theoretically treating magnetically ordered systems. Thus, whereas the neutron form factors obtained from band-structure calculations[1] for the ferromagnetic metals are not in good agreement with experiment,[2] it has been rather puzzling that the Hartree-Fock free-ion spin densities for the +2 state of ionization have the same shape as those determined from experiment.

The accurate determination of the neutron magnetic form factor of paramagnetic Pd metal by Cable *et al.*[3] has shown that the magnetization-density contraction is more pronounced than that observed for the 3*d* ferromagnets. Using the same analysis[2] as previously carried out for the ferromagnets, Cable *et al.* find asymmetry parameters which agree with those found for Ni metal but a local-moment density which is contracted by about 15% relative to the Hartree-Fock Pd^{2+} density function (which is already contracted by the same amount relative to the neutral free atom). This determination of the field-induced magnetic form factor of Pd metal provides a timely and meaningful challenge to theory.

We report in this Letter the results of augmented-plane-wave (APW) calculations on Pd metal which have yielded the first theoretical determination of an induced neutron magnetic form factor for a paramagnetic metal from *ab initio* solid-state *wave functions*. In contrast to earlier work on the ferromagnetic metals, the results are found to be in excellent agreement with the recent experiments of Cable *et al.*[3] A remarkable fea-