Investigation of the Paramagnetic Neutron Scattering from Metallic Palladium*

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Neutron paramagnetic scattering measurements were made for metallic palladium at sample temperatures of 15, 77, and 298°K. Within experimental error the paramagnetic scattering cross section is the same for these temperatures and is only about 5 mb/sr atom. It is concluded that the Pd $4d^9$ spin states exist for a time short relative to the time of passage of a neutron over an atom ($\sim 10^{-13}$ sec for a 1-Å neutron).

INTRODUCTION

IN principle, the magnetic scattering of neutrons from transition metals in the paramagnetic state should provide information regarding their electronic structures. Such measurements have been made for Fe and Ni [1] but their interpretation is complicated by the existence of short-range correlation effects which persist up to very high temperatures. This problem should not be encountered in the case of Pd since this metal does not order magnetically. An experiment was therefore undertaken in an attempt to measure the paramagnetic scattering of 1.092-Å neutrons from Pd.

EXPERIMENTAL PROCEDURE

The sample was filed to 100 mesh particle size and heat treated at 700°C for 8h in a vacuum to ensure the absence of hydrogen, which has an appreciable anisotropic incoherent cross section. After furnace cooling the sample was loaded into a rectangular aluminum cell and mounted into an exchange gas chamber cryostat. Neutron scattering data were obtained at fixed sample temperatures of 298, 77, and 15°K using neutrons of 1.092-Å wavelength along with Pu and Ir filters to remove the second- and third-order beam contaminants. Calibration was made with a standard Ni sample.

EXPERIMENTAL RESULTS

The observed room-temperature diffuse-scattering cross section for the sample is shown in Fig. 1. These data have been corrected for background scattering effects by the usual Cd difference technique[2] and therefore represent scattering only from the sample. This includes multiple, incoherent, and thermal diffuse scattering as well as any paramagnetic scattering that might be present. The multiple scattering cannot be accurately calculated but is not believed to be an important contribution to the diffuse scattering in the present experiment. This conclusion is based on measurements carried out on a series of cylindrical samples of Pd filings of varying effective volume for which the estimated[3] multiple scattering varied from 18 to 31 mb/sr atom. Within experimental error the observed cross sections were the same as that observed in the present experiment ($\sim$44 mb). The incoherent scattering should be readily calculable but unfortunately the cross section is not well established. [$\sigma_s = 4.8 \pm 0.3$ b,[4] of which 4.4 b is coherent.] The multiple and incoherent scattering, though not readily evaluated, are expected to be independent of scattering angle and may be considered collectively as an isotropic background which can be evaluated if the angularly dependent terms can be separated. This separation was achieved by assuming that, because of the rapid decrease of the Pd $4d$ form factor with scattering angle, there is no paramagnetic contribution to the background at $\sin\theta/\lambda$ values larger than 0.3 Å^{-1}. The only anisotropic term at large angles is then the thermal diffuse scattering which is given by

$$d\sigma/d\Omega(\text{thermal diffuse}) = b_0^2(1 - e^{-2W \sin^2\theta/\lambda^2})$$

in which b_0 is the Pd scattering amplitude and W is the Debye-Waller factor. The scattering amplitude of Pd was determined from the intensities of the first five Bragg reflections with thermal corrections being

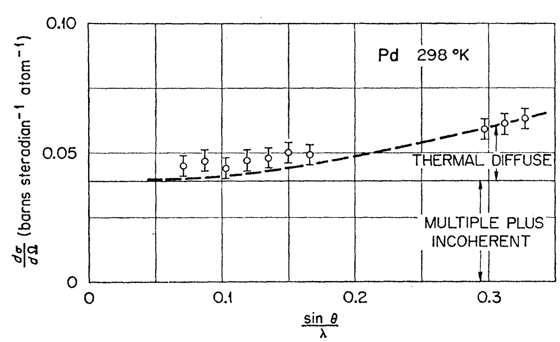

FIG. 1. Diffuse-scattering cross section of Pd at 298°K. For scattering angles in the $\sin\theta/\lambda = 0.3$-Å^{-1} region there is assumed to be no paramagnetic scattering. The multiple and incoherent scattering are assumed isotropic and the thermal diffuse scattering is calculated with $\theta_D = 315$°K. The difference between the data points and the dashed curve represents the paramagnetic scattering.

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TABLE I. Evaluation of the isotropic scattering cross section. (Multiple+incoherent scattering).

T (°K)	Θ_D (°K)[a]	$2W$	$\frac{d\sigma}{d\Omega}$ (thermal diffuse)[b]	$\frac{d\sigma}{d\Omega}$(obs)[c]	$\frac{d\sigma}{d\Omega}$(multiple +incoherent)
15	275	0.203	0.007	0.045	0.038±0.004
77	315	0.236	0.008	0.046	0.038±0.004
298	315	0.663	0.022	0.061	0.039±0.006
			±2%	±7%	

[a] B. W. Veal and J. A. Rayne, Phys. Rev. **135**, A442 (1964).
[b] $d\sigma/d\Omega$(thermal diffuse) $=b_0^2[1-\exp(-2W\sin^2\theta/\lambda^2)]$, $b_0^2=0.349$, $\sin\theta/\lambda=0.312$.
[c] $\sin\theta/\lambda=0.312$.

made by use of $\theta_D=275$°K for the 15°K data and $\theta_D=315$°K for the 77 and 298°K data.[5] The results for the three temperatures were in excellent agreement and yielded a value of b_0(Pd)$=0.591\pm0.006\times10^{-12}$ cm in good accord with previously reported[6,7] values of 0.58 ±0.04 and $0.59\pm0.03\times10^{-12}$ cm. The evaluation of the isotropic scattering level at $\sin\theta/\lambda=0.312$ is given in Table I in which the calculated thermal diffuse scattering and the observed diffuse scattering are given in columns 4 and 5, respectively. The difference, which corresponds to the isotropic scattering level, is given in column 6 and the agreement obtained at the three temperatures would seem to justify the thermal correction factors that were used (columns 2 and 3).

The paramagnetic scattering, which should appear at smaller scattering angles, may be taken as the difference between the data points and the dashed curve in Fig. 1. This paramagnetic scattering is represented by the data points in Fig. 2 and also is presented in Table II. In the table, all of the small-angle data have been averaged as though taken at a $\sin\theta/\lambda$ value of 0.119 Å^{-1}. After correction for thermal diffuse, multiple, and incoherent scattering the remaining paramagnetic scattering cross section is only about 5 mb/sr atom.

TABLE II. Evaluation of the paramagnetic-scattering cross section.[a]

T (°K)	$\frac{d\sigma}{d\Omega}$(obs)	$\frac{d\sigma}{d\Omega}$ (thermal diffuse)	$\frac{d\sigma}{d\Omega}$ (multiple +incoherent)	$\frac{d\sigma}{d\Omega}$ (paramagnetic)
15	0.042	0.001		0.003
77	0.043	0.001	0.038	0.004
298	0.049	0.003		0.008
	±0.001		±0.003	±0.003

[a] All cross sections evaluated at $\sin\theta/\lambda=0.119$.

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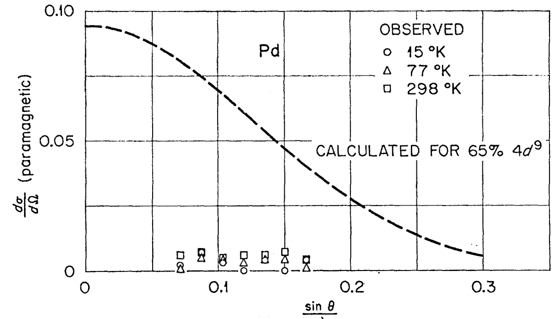

FIG. 2. Paramagnetic-scattering cross section of Pd at 15, 77, and 298°K. The dashed curve is calculated for 65% $4d^9$ states with $S=\frac{1}{2}$ and the Freeman-Watson Pd^{+2} form factor (Ref. 9).

DISCUSSION

The high-temperature magnetic-susceptibility data for Pd exhibit a Curie-Weiss dependence which has been interpreted on the basis of a model with 65% $4d^9$ and 35% $4d^{10}$ states.[8] For such a model the paramagnetic-scattering cross section is given by

$$d\sigma/d\Omega(\text{paramagnetic})=0.65(e^2\gamma/mc^2)^2\tfrac{2}{3}f^2S(S+1)\,,$$

provided that these states remain well defined during the time of passage of a neutron over an atom ($\sim10^{-13}$ sec for 1-Å neutrons). This cross section with $S=\frac{1}{2}$ and the Freeman-Watson Pd^{+2} form factor[9] is shown as the dashed curve in Fig. 2. The low observed cross section relative to the calculated curve indicates that the localization of the spin moment on a given atom exists for a time short compared with the neutron-passage time.

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