Direct Observation of Paramagnons in Palladium

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We report an inelastic neutron scattering study of the spin fluctuations in the nearly ferromagnetic element palladium. Dispersive over-damped collective magnetic excitations or ''paramagnons'' are observed up to 128 meV. We analyze our results in terms of a Moriya-Lonzarich–type spin-fluctuation model and estimate the contribution of the spin fluctuations to the low-temperature heat capacity. In spite of the paramagnon excitations being relatively strong, their relaxation rates are large. This leads to a small contribution to the low-temperature electronic specific heat.

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Nearly ferromagnetic metals are of topical interest because their bulk electronic properties can be modified by the presence of spin fluctuations [1–5]. Doniach pointed out [1] that metals close to ferromagnetic order at zero temperature should show dispersive over-damped magnetic excitations or ''paramagnons.'' These should be contrasted with the well-defined propagating spin waves which occur in an ordered ferromagnetic phase. Over-damped modes are still important because they are excited with increasing temperature and therefore contribute to the electronic specific heat [1–5]. It has also been suggested that they can mediate superconductive pairing [6,7]. In this paper, we report an inelastic neutron scattering (INS) study of paramagnons in the element palladium. Pd is unique among the paramagnetic elements in that it shows a large and temperature-dependent susceptibility [8]. It has one of the highest densities of states (DOS) [9–12] at the Fermi energy of the d-band metals, and the measured susceptibility is approximately 10 times larger than that calculated directly from the DOS. Thus it is a good system in which to search for paramagnons. We find that the paramagnon excitations can be observed over a wide range of energies between 25 and 128 meV in the present experiment.

Palladium is a face-centered-cubic metal with lattice parameter $a = 3.88$ Å. We studied a 487 g single crystal of approximately cylindrical shape with a mosaic of approximately 1.5° FWHM. Prior to the experiment the crystal was annealed at a temperature of 300 °C under a vacuum of approximately 10^{-6} torr for 72 h to expel hydrogen [13]. Figure 1 shows the susceptibility of a piece cut from our sample compared to a powder standard. Both the reference sample and the single crystal used in the experiment show an upturn in the susceptibility at low temperatures. It is known that even small concentrations of magnetic impurities such as Fe can cause such an upturn at low temperatures [11] due to paramagnetism of the Fe ''giant moments'': based on the magnitude of the upturn, we estimate the concentration of magnetic impurities to be 60–90 ppm. The magnetic impurities can also affect the low-temperature specific heat below $T \lesssim 5$ K [14]. In order to avoid any possible complications associated with the low-temperature spin freezing, we collected data at $T = 20$ K and above [15].

INS experiments were performed on the MARI instrument at the ISIS spallation source. MARI is a low-background, direct-geometry, time-of-flight chopper spectrometer. For the present experiment, we used detectors located in a single plane, henceforth known as the scattering plane. The $(1\bar{1}0)$ crystal plane was mounted coincident with the scattering plane for the present experiment, allowing wave vectors of the type $\mathbf{Q} = (h, h, \ell)$ to be investigated. INS probes the E and $\mathbf{Q}$ dependence of $\chi''(\mathbf{Q}, \omega)$. The magnetic cross section is given by

$$\frac{d^2\sigma}{d\Omega dE} = \frac{2(\gamma r_e)^2}{\pi g^2 \mu_B^2} \frac{k_f}{k_i} |F(\mathbf{Q})|^2 \frac{\chi''(\mathbf{Q}, \hbar\omega)}{1 - \exp(-\hbar\omega/kT)}, \quad (1)$$

where $(\gamma r_e)^2 = 0.2905$ b sr^{-1}, $\mathbf{k}_i$ and $\mathbf{k}_f$ are the incident and final neutron wave vectors, and $|F(\mathbf{Q})|^2$ is the magnetic form factor for a Pd 4d orbital [16]. Data were placed on an absolute scale using a vanadium standard and measurements of the acoustic phonons of the sample. The relatively large size of the Pd crystal meant that the incident beam

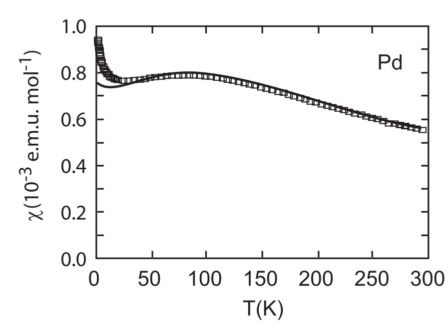

FIG. 1. The bulk susceptibility of the Pd single crystal used in the present experiment (squares) compared to a standard powder.

was attenuated by absorption and Bragg scattering within the sample. We carried out Monte Carlo simulations of these effects to account for them in our fitting procedure. We use the reciprocal lattice to label wave vectors, $\mathbf{Q} = h\mathbf{a}^\star + k\mathbf{b}^\star + l\mathbf{c}^\star$.

Figure 2 shows data collected for $T = 20$ K with an incident energy $E_i = 71$ meV with the [110] direction parallel to $\mathbf{k}_i$. The main panel shows the scattering function $(k_i/k_f)(d^2\sigma/d\Omega dE)$ plotted as a function of the wave vector of the excitations $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$. Because the data are collected in a single setting, the energy of the excitations probed, $\hbar\omega = E_i - E_f$, varies over the figure. The energy transfer corresponding to each wave vector can be determined from the inset of the figure. At low energies below about 30 meV, we observe the highly structured phonon scattering. Above the highest phonon energy we observe additional scattering near the $\mathbf{Q} = (1, 1, -1)$ reciprocal-lattice position. For the present setting this corresponds to $\hbar\omega = 39$ meV. Figure 3(b) shows a cut directly through this position, demonstrating that the additional scattering is peaked at $\mathbf{Q} = (1, 1, -1)$. We note that there is no observable scattering at the $(2, 2, -2)$ reciprocal-lattice position with larger $|\mathbf{Q}|$. This is consistent with the drop in $|F(\mathbf{Q})|^2$ by a factor of more than 100 [16] expected for magnetic scattering. Figure 3(a) shows that the response near the $(11\bar{1})$ zone center is also present at lower energies. Indeed it is peaked at either side of $(11\bar{1})$. Figure 4 shows data collected at $T = 300$ K for incident energies $E_i = 35.4$, 71, 204.3, 300 meV. The scattering near the zone center positions of (111) and (002) types persists up to the highest energies investigated in the present experiment, $\hbar\omega = 128$ meV. It is interesting to note that the width of the response is not resolution limited [the horizontal bars in Figs. 4(a)–4(d) represent the instrumental resolution] and it broadens with increasing energy transfer. It can also be seen that the observed response is often not symmetric across the reciprocal-lattice point [e.g., Fig. 4(b)]. This is because of the rapid variation of $|F(\mathbf{Q})|^2$ across the cut and is generally accounted for in the analysis below.

It is hard to see how the observed scattering can be due to anything other than collective magnetic excitations. The background of the present experiment is dominated by scattering from the sample. We were unable to identify a multiple scattering mechanism which could produce a strong response near $\mathbf{Q} = (1, 1, 1)$ for *all* energy transfers and incident energies. For example, Bragg plus phonon scattering produces a structured response below the phonon cutoff energy (29 meV), and multiple phonon scattering produces a diffuse response over a wide range of $\mathbf{Q}$. When a strong scatterer (vanadium) is introduced at the sample position, similar results are not observed. The

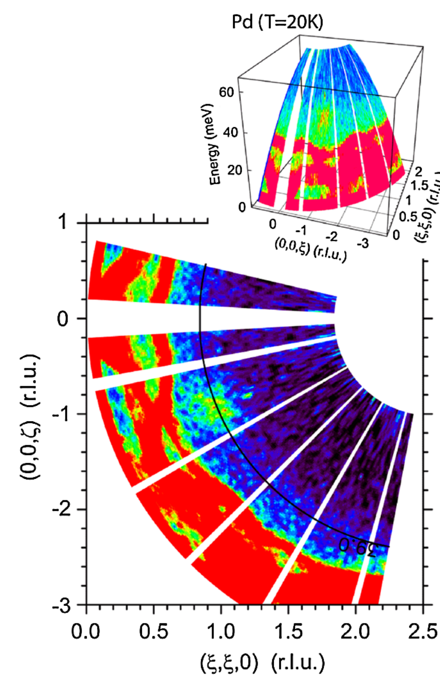

FIG. 2 (color online). Paramagnon excitations in Pd at $T = 20$ K. Data are collected for a single spectrometer setting with $E_i = 71$ meV. Excitations are probed over the surface of $\mathbf{Q}$-ω space shown in the inset. Phonons are observed at lower energies $\hbar\omega \lesssim 30$ meV. The paramagnon scattering can be seen near $\mathbf{Q} = (1, 1, -1)$, which corresponds to 39 meV. The black arc is the $\hbar\omega = 39$ meV contour. The units of the plot are mb st^{-1} meV^{-1} f.u.$^{-1}$ (f.u. denotes formula unit).

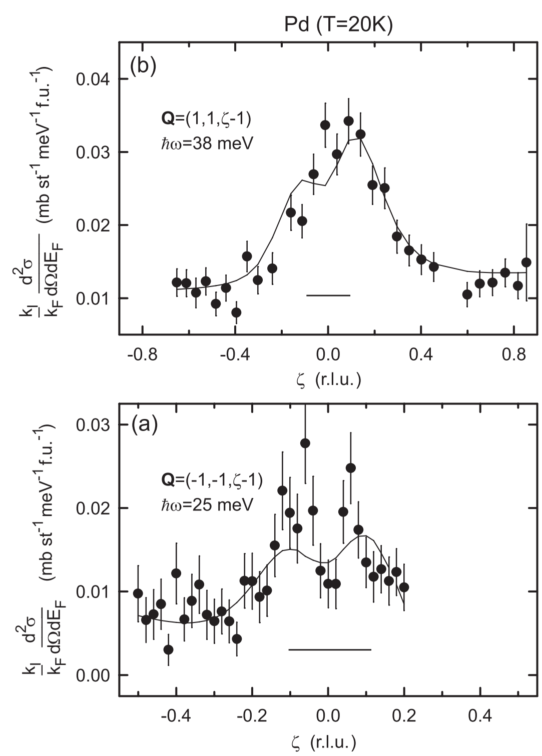

FIG. 3. Paramagnon excitations at $T = 20$ K. Cuts along $(0, 0, \zeta)$ through the (111) reciprocal-lattice position with $E_i = 35$ (a) and 71 meV (b) are shown. The integrated proton current delivered to the target during the run was 3500 μAh. Horizontal bars denote (FWHM) resolution.

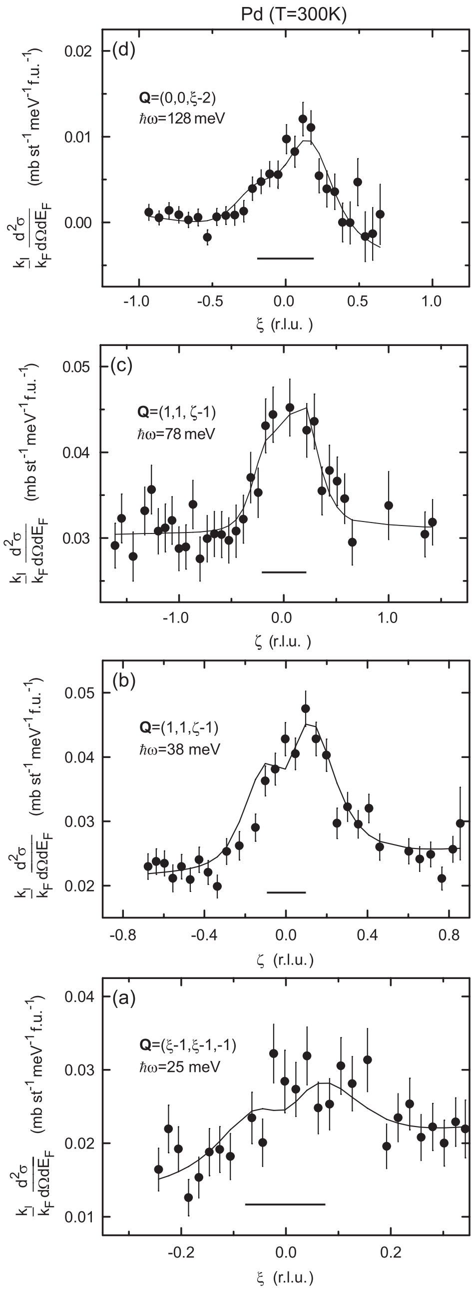

FIG. 4. Paramagnon excitations at $T = 300$ K. Cuts through the (111) and (200) reciprocal-lattice points are shown. Incident energies used were $E_i = 35$ (a), 71 (b), 204 (c), and 300 meV (d). For (a), (b), and (d), data were collected at a constant scattering angle. Solid lines are fits to Eqs. (1)–(4). The unit r.l.u. denotes reciprocal-lattice unit.

observed Pd response also decreases with $|\mathbf{Q}|$ as $|F(\mathbf{Q})|^2$, as would be expected for magnetic scattering.

Magnetic excitations in nearly ferromagnetic and weakly magnetic metals are usually interpreted in terms of correlated particle-hole pairs (Stoner excitations). Doniach [1] calculated the interacting spin susceptibility for a nearly ferromagnetic metal using the RPA formulation of Izuyama *et al.* [17], for a single-band Hubbard model. Moriya [3] and Lonzarich [4,5] (ML) developed a generalized phenomenological form which can be used to describe nearly ferromagnetic metals and provides a useful input to spin-fluctuation theories. In the ML model the imaginary part of generalized susceptibility [18] takes the form

$$\chi''(q,\omega) = \frac{\chi(q)\omega\Gamma(q)}{\Gamma^2(q)+\omega^2}, \tag{2}$$

where the relaxation rate $\Gamma(q)$ is given by

$$\Gamma(q) = \gamma q \chi^{-1}(q) \tag{3}$$

and the wave-vector–dependent susceptibility $\chi(q) = \chi(q, \omega = 0)$ is given by

$$\chi^{-1}(q) = \chi^{-1} + cq^2. \tag{4}$$

The above expansions are valid in the small $q = |\mathbf{q}|$ limit, and $\mathbf{q}$ is measured from a reciprocal-lattice point. Within this model the response is characterized by three microscopic parameters, c, γ, and χ, of which only the susceptibility is temperature dependent.

We first fitted our $T = 300$ K data to Eqs. (1)–(4). The solid lines in Fig. 4 are the results of our fits. Because the bulk susceptibility of Pd is well known, we fixed this parameter and allowed an overall scale factor to take up any errors in the absolute normalization. We found this factor to be 0.8 ± 0.2, i.e., unity within the error of the experiment. The results of fitting the model to the $T = 300$ K data are shown in Table I. Within the ML model only the susceptibility is expected to vary significantly with temperature. The lines in Fig. 3 show the predictions of the model using the $T = 20$ K value of the susceptibility from Fig. 1. It is interesting to note that the response at the lowest energy (25 meV) is slightly sharper than the model predicts. The doubled peaked structure seen in Fig. 3(a) is a consequence of the ML model, because $\Gamma(q) \to 0$ as $q \to 0$, and does not indicate propagating excitations. In spite of being a small q and ω model, the phenomenological ML model appears to provide a reasonable global description of the data. The parameters in Table. I can be estimated from electronic structure calculations [10–12]. The calculated values are $\hbar\gamma = 2.1$ [11] and 1.1 μ_B^2 meV^{-1} [12] and $c = 836$ [10], 900 [11], and 925 μ_B^{-2} Å^2 meV [12]. It is not clear why there is a significant discrepancy in the estimation of c. However, it has been noted that c is very sensitive to the detailed band structure near the Fermi energy [11,12].

The present results can be compared with those obtained on Ni_3Ga. This material is closer to ferromagnetic order at low temperatures and shows a susceptibility enhancement of about 100 with respect to simple band structure calculations [20]. Unfortunately, large single crystals of Ni_3Ga are not available. Bernhoeft *et al.* [19] carried out an INS study on polycrystalline material at low energies and found that the response could be parametrized using the model used here. The parameters found are shown in Table I. The paramagnon excitations in Ni_3Ga are observed at much

TABLE I. The results of fitting the phenomenological ML model [Eqs. (2)–(4)] to our data [18]. The susceptibility quoted for Pd is for $T = 20$ K. The results [19] of a similar analysis for Ni_3Ga are also given.

	$\hbar\gamma$ (μ_B^2 Å f.u.$^{-1}$)	c (μ_B^{-2} Å meV f.u.)	χ^{-1} (μ_B^{-2} meV f.u.)
Pd	1.74 ± 0.80	294 ± 130	41.1
Ni_3Ga	2.6	116	2.0

lower energies than in Pd: the maximum energy investigated was a few meV. Surprisingly, the γ and c parameters in the two materials are the same to within a factor of about 2. The energy scale of the spin fluctuations is controlled almost entirely by the susceptibility χ, which is different in the two materials.

As mentioned in the introduction, we would expect [2,3,5,21,22] that the presence of paramagnons will contribute to the low-temperature linear specific heat $C = \gamma_C T$. We may use our phenomenological response to estimate the contribution of spin fluctuation to the low-temperature specific heat in Pd. Within the ML model [5], the electronic specific heat has been estimated to be

$$C = \gamma_C T + \delta T^3 \ln(T/T^\star), \tag{5}$$

where

$$\gamma_C = \frac{k_B^2}{4\pi\hbar\gamma c} \ln(1 + c\chi q_u^2), \tag{6}$$

$\delta = 2\pi k_B^4 \chi^3/(5\hbar^3\gamma)$, and $T^\star \approx \hbar\gamma/(k_B c^{1/2}\chi^{3/2})$. Using our values for c, γ, and χ and a cutoff wave vector q_u at the Brillouin zone boundary ($q_{\mathrm{BZ}} = 1.71$ Å^{-1}), we obtain an estimate of the electronic specific heat of $\gamma_C = 5.0 \pm 2.7$ mJ K^{-2} mol^{-1}. This should be compared with that obtained directly from the band structure using the standard relation $\gamma_C = (\pi^2/3)k_B^2 N(\varepsilon_F)$ and the calculated $N(\varepsilon_F) = 32.7$ states atom^{-1} Ry^{-1} [9], which yields $\gamma_C = 5.6$ mJ K^{-2} mol^{-1}. We should also note that enhancement of the linear specific heat due to electron-phonon coupling is estimated to lie in the range 28%–41% [23,24] for Pd, and the experimentally determined value is $\gamma_C = 9.42$ mJ K^{-2} mol^{-1} [14,15,25]. Combining these facts [26] suggests that the enhancement in the electronic specific heat due to spin fluctuations in Pd is in the range 30%–40% which is within the uncertainty range of our estimate based on the ML model. Note the estimation based on the ML model is determined only by experimentally measured quantities. Thus we have a consistent picture in which the observation of strongly spin fluctuations in Pd does not lead to a large contribution to the linear specific heat.

In summary, we have used inelastic neutron scattering to measure so-called paramagnon excitations in palladium. Paramagnons are dispersive over-damped collective excitations which are present in nearly ferromagnetic metals. We observe a dispersing response which is strong near the Brillouin zone center and broadens in wave vectors with increasing energy up to the highest energies investigated, $\hbar\omega = 128$ meV. We parametrize the observed response and use a Moriya-Lonzarich spin-fluctuation model to estimate the low-temperature linear specific heat directly from our data. We find that a relatively small enhancement of the specific heat observed in Pd is consistent with the observed paramagnon spectrum, which is broad in energy compared to more strongly enhanced systems such as heavy fermions [27].

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