Magnetic Field Dependence of the Electronic Specific Heat of Palladium

T. Y. Hsiang, J. W. Reister, and H. Weinstock
Department of Physics, Illinois Institute of Technology, Chicago, Illinois 60616

and

G. W. Crabtree
Argonne National Laboratory, Argonne, Illinois 60439

and

J. J. Vuillemin
University of Arizona, Tucson, Arizona 85721

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Specific heat of the enhanced paramagnetic material palladium was measured in magnetic field up to 11 T. The fitted value of the electronic-specific-heat coefficient γ was found to decrease from 9.36 mJ/mole K^2 at zero field to 8.63 mJ/mole K^2 at 11 T, but we did not observe a field dependence of the Debye temperature θ_D. We attribute our findings to the paramagnon effect in palladium.

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In this Letter we report the measurement of the specific heat of palladium in magnetic fields up to 11.0 T. This experiment was motivated by the findings of Dye *et al.*[1] in the de Haas–van Alphen measurements of palladium. These authors measured the Fermi surface and cyclotron mass of Pd in a magnetic field up to 13 T and at 0.35 K. They found the average electron density of states at the Fermi surface, $N(0)$, to be 14% less than the value deduced from specific-heat measurements[2] in zero field. In other materials, such as niobium,[3] there was an excellent agreement between the de Haas–van Alphen and specific-heat results. While the difference found in Pd may be attributable to many sources, it was noted that since Pd has a large Stoner enhancement factor S in comparison with other elements, one possible explanation is that the high magnetic field used for the de Haas–van Alphen experiments effectively quenched some of the electron-paramagnon enhancement of $N(0)$. Our experiment was intended to test this idea.

The first theoretical effort to compute the specific heat of strongly paramagnetic systems was made in 1966.[4,5] It was found that the low-temperature specific heat can be expressed as

$$C=\gamma T[\alpha+c(T/T_{\mathrm{SF}})^2\ln(T/T_{\mathrm{SF}})]+\beta T^3, \qquad (1)$$

where γ is the free-electron specific-heat coefficient, α is defined to be $(1+\lambda_{\mathrm{ph}}+\lambda_m)$ and contains both the electron-phonon enhancement λ_{ph} and the electron-paramagnon enhancement λ_m, βT^3 is the usual phonon contribution, and $c\equiv S(1-S^{-1})^2\simeq S$. The spin-fluctuation temperature T_{SF} is defined as T_F/S, where T_F is the degeneracy temperature.

Equation (1) provides a good fit to the experimental data[6] for liquid ^{3}He and there is some evidence that this equation may explain the observed specific-heat anomaly of the C-15 compound UAl$_2$.[7] The difficulties in comparing the paramagnon theory to the specific-heat data of *solids* are twofold: The effect of magnetic impurities is difficult to distinguish from the paramagnon contribution at low temperatures, and the deviation of the phonon term from the simple T^3 form also masks the logarithmic term in Eq. (1).

A more clear-cut way to separate the paramagnon effect was first pointed out by Brinkman and Engelsberg[8]: If a magnetic field of magnitude $H \gtrsim k_B T_{\mathrm{SF}}/g\mu_{\mathrm{B}}$ is applied to the material, the Zeeman splitting of the energies of the spin-up and spin-down electronic states is large enough for the electrons and paramagnons to be decoupled, quenching the paramagnon contribution in Eq. (1). However, an estimate of the magnitude of the magnetic field reqired to effect this quenching (taking T_{SF} of Pd to be 250 K and g to be 2) shows that a field of 190 T is needed!

More quantitative calculations of the effect of magnetic fields were done by Béal-Monod, Ma, and Fredkin.[9] They found the change in C to be given by

$$\frac{\Delta C(H)}{C(0)}\equiv\frac{C(0)-C(H)}{C(0)}\simeq 0.1\left(\frac{g\mu_{\mathrm{B}}H}{k_B T_{\mathrm{SF}}}\right)^2\frac{S}{\ln S}. \qquad (2)$$

Based on these theories, a conveniently achievable field of, for example, 10 T, would produce about 0.1% change in the specific heat of Pd.

More recently, Hertel, Appel, and Fay[10] pointed out that the previous calculations tacitly assumed a momentum-independent exchange potential which is well known to grossly overestimate the mass enhancement factor.[11] Hertel, Appel, and Fay used instead a q-dependent exchange potential of the form suggested by Fay and Appel,[12]

$$I(q)=Ia^2/(a^2+q^2), \tag{3}$$

where a is a parameter of the order of the Fermi vector. The magnitudes of I and a are obtained by fitting the theory to the experimental values of the enhanced susceptibility and the mass enhancement factor. Using $S=10$ and $\lambda_m=0.37$ for palladium, these authors estimated $a\cong 0.7k_F$. The important consequence here is that, with a q-dependent exchange, the effect of magnetic fields in reducing the paramagnon enhancement is much more pronounced at low field values. At a field of 10 T, Hertel, Appel, and Fay computed $\Delta C(H)$ to be nearly an order of magnitude larger than the prediction of Béal-Monod, Ma, and Fredkin.

The model of Hertel, Appel, and Fay is clearly more realistic than the earlier models. It indicates that a modest level of magnetic field can be used to check the paramagnon theory in Pd. However, the theory does not consider anisotropy effects in $I(\vec{q})$, nor does the parabolic band approximation used in the theory properly treat the unusual electronic-structure and Fermi-surface properties of Pd. Therefore any comparison with experiment should be taken to be qualitative only.

The Pd sample used in our experiments was prepared from 99.999% pure Pd sponge purchased from Johnson Mathey. Impurities of Fe, Ni, and Co were claimed to be less than 1 ppm total. Repeated zone refining in air[13] brought the residual resistivity ratio ($R_{300}/R_{4.2}$) to over 10 000. The sample was composed of several 1-mm-diam rods sintered together to form a cylindrical bundle. The total weight was about 18.6 g. The sample was mounted in a dilution refrigeration system containing a superconducting magnet that operates in the persistent mode up to 11.5 T. Our data were taken at 0, 5.0, 7.0, 9.0, and 11.0 T.

The heat capacity was measured with use of a heat-link method.[14] A capacitance thermometer mounted on a heat sink was calibrated against a Ge thermometer and a carbon glass thermometer. A ground-down carbon thermometer was placed on the sample holder as the temperature sensor and was calibrated against the capacitance thermometer. A 350-Ω strain gauge was used as the sample heater. The heat link was a 99.999% pure copper ribbon which provided a time constant of 20 to 200 sec. When a heat pulse was applied, the pulse current and voltage and the decay of the sample temperature were simultaneously recorded to provide a direct measure of the heat capacity.[14] The technique was checked with a copper sample and agreement with the published data[15] was within 2% for all field values. The sensitivity of our capacitance thermometer is poor below 0.2 K, as indicated by the large scatter of data in this temperature range. We consider these data unreliable.

Figure 1 shows the specific heat of our Pd sample at two extremal field values from 0.2 to ~11 K. There is an apparent nonlinearity in this C/T vs T^2 plot. This could indicate either that the phonon contribution to C deviates from the form of T^3, or that it is the result of the logarithmic term in Eq. (1), or probably both. The best fit to the data, however, is found with a simple polynomial:

$$C=\gamma T+BT^3+DT^5. \tag{4}$$

The fitted values of γ, B, and D at all field values are listed in Table I. An attempt to fit the data to Eq. (1) produces a poor fit and large scatter in the values of $T_{\rm SF}$. We are forced to con-

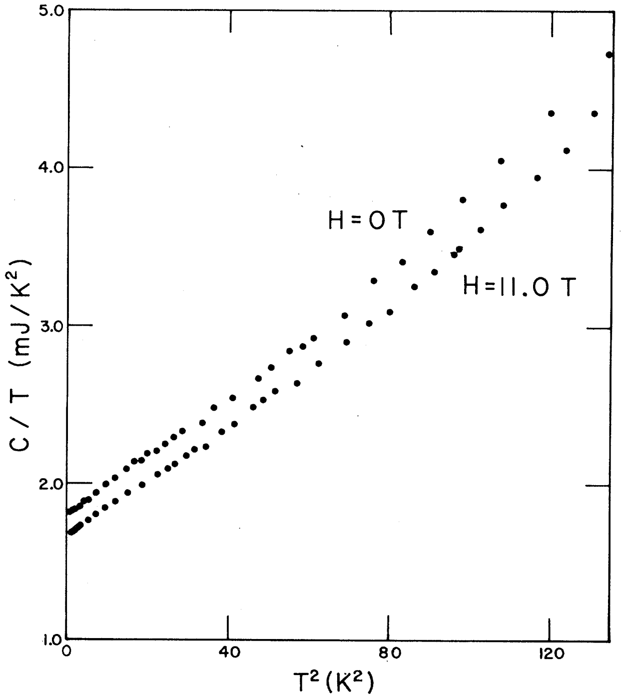

FIG. 1. Specific-heat data at zero field and $H = 11.0$ T.

TABLE I. Fitted values of the specific-heat coefficients. The terms γ, B, and D are defined in Eq. (4).

H (T)	γ	B ($\times 10^{-5}$)	D ($\times 10^{-2}$)
0	9.36 ± 0.05	9.70	6.5
5	9.09 ± 0.08	9.65	7.1
7	8.90 ± 0.08	9.63	5.8
9	8.81 ± 0.08	9.81	6.2
11	8.63 ± 0.08	9.55	4.2

clude that our data are not adequate to serve as a check of the logarithmic term in Eq. (1). At the low-temperature end, no apparent "upturn" of C/T was observed down to $T \simeq 0.2$ K.

The zero-field values of γ and θ_D are 9.36 ± 0.05 mJ/mole K^2 and 272 ± 3 K, respectively. These are in reasonable agreement with previous work.[2]

Our central results are shown in Fig. 2. We found γ to decrease with increasing magnetic field by as much as 7.8% at 11.0 T while there is no systematic variation of θ_D. It is important to consider the various possibilities for the decrease of γ.

It is well known that a small amount of a magnetic impurity can contribute significantly to the specific heat at low temperatures[16] and that this contribution can be quenched with a magnetic field.[17] We checked this possibility by comparing the fitted values of γ at different magnetic field with the values of C/T at a specific low temperature, 0.5 K. The values of C/T fell within the error bars of γ in Fig. 2. The effect of magnetic impurities, on the other hand, would cause an increase in C/T over the fitted γ at small values of T^2. In addition, since the energy associated with the local spin fluctuation[16] due to the impurity is k_BT, it thus takes a field of $H \geqslant k_BT/g\mu_B = 0.75$ T (at 1 K) to quench the local spin fluctuation completely. The observed suppression of γ (Fig. 2) persisted to much higher field strength. We conclude, therefore, that the effect of magnetic impurities is not important.

Another possibility for the change in γ is the band-structure effect. If one assumes that the bands are rigidly split by the magnetic field and calculates the change in $N(0)$ using the values computed by O. K. Anderson,[18] one deduces that there would be a slight ($<0.1\%$) increase in $N(0)$ at 11 T—hence an increase in γ. More recently, Jarlborg and Freeman[19] calculated directly the change in $N(0)$ in a magnetic field, using a self-consistent scheme which takes into account the magnetic energy of the electrons. They found that at 11 T, $N(0)$ would decrease from the zero-field value by about 0.5%. The experimentally observed change in γ is of an order of magnitude larger than the prediction based on the band-structure effects. Although all the above-mentioned calculations did not take into account the spin-orbit coupling in palladium, it seems unlikely that this would change the results by an order of magnitude.

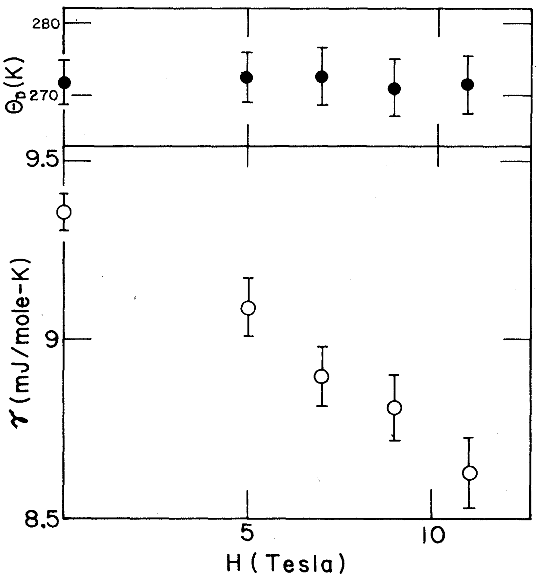

FIG. 2. Fitted value of γ and θ_D for palladium at several values of magnetic field.

It is tempting to attribute the dependence of $\gamma(H)$ to the effect of paramagnons. The calculation by Hertel, Appel, and Fay[10] shows that effects comparable to our result are reasonable. For example, if the value of a is reduced to $0.45k_F$ in Eq. (3), a 4.5% effect is predicted. In addition, three recent experiments are consistent with our findings. For LuCo$_2$ (a spin-fluctuation system with $S \cong 10$),[20] a larger suppression of γ was observed at $H = 10$ T; for Sc$_3$In,[21] an itinerant-electron ferromagnet with $T_c = 6$ K, the anomaly in heat capacity above the ordering temperature was quenched with a magnetic field; in the mixed-valence compound CeSn$_3$,[22] both γ and θ_D were found to be field dependent. However, we should point out that there is a discrepancy between our findings and that of the de Haas–van Alphen experiments.[1] In addition, the magnetization measurement of Pd up to $H = 30$ T by Muller, Gersdorf, and Roeland[23] did not uncover a nonlinearity of more than 2% in the susceptibility. Clearly, more theoretical and experimental investigations are required to clarify the inconsistency among these presumably related experiments.

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Momentum Transfer Cutoff in the Scattering of Neon Atoms from a Nickel (111) Surface

B. Feuerbacher
Space Science Department of the European Space Agency, European Space Research and Technology Centre, 2200-AG Noordwijk, The Netherlands

and

R. F. Willis
Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom

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Angle-resolved time-of-flight measurements of inelastic scattering of Ne atoms from a Ni(111) surface show an effective interaction radius increased with respect to the Ne hard-sphere radius, such that the Ne atoms impact against five Ni atoms. This limits the interaction with acoustic surface waves to some critical cutoff wave vector, K_c. Larger energy transfers are accompanied by vanishing momentum transfer as assumed in a cubes model.

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A gas atom (or molecule) colliding with a solid exchanges energy and momentum with the surface. The incident particle may be scattered elastically, inelastically, or it may become trapped at the surface, depending on the amount of energy transferred. The exchange of energy and momentum is therefore of fundamental importance for all processes involving dynamic gas-surface interactions. It is usually described phenomenologically in terms of an energy accommodation coefficient,[1,2] while the underlying microscopic processes are still a matter of current debate.

Measurements of He scattering from alkali halide surfaces[3] have shown that the interaction with single Rayleigh surface phonons is the predominant energy-transfer process between light