Evidence for the Existence of Long-Range Magnetic Ordering in a Liquid Undercooled Metal

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Liquid $\mathrm{Co}_{100-x}\mathrm{Pd}_x$ alloys were undercooled below the Curie temperatures $T_C(s)$ of the ferromagnetic solid phase by using electromagnetic levitation. A modified Faraday balance was applied to measure the magnetization of the undercooled liquid sample as a function of temperature. A Curie-Weiss behavior is detected. The Curie temperature $T_C(l)$ is determined for the transition from the paramagnetic to the ferromagnetic state of this metallic liquid with long-range magnetic order. $T_C(l)$ is slightly smaller than $T_C(s)$.

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So far, experimental experience has shown that the existence of magnetic long-range order as, for example, present in ferromagnets is restricted to the solid state of matter. The only exception was the superfluid A1 phase of ^{3}He below 2.7 mK [1,2]. Within the Heisenberg model the magnetic exchange energy between the ions carrying a local magnetic moment strongly depends on the interatomic distance. The exchange energy leads to magnetic long-range order at temperatures below the Curie temperature T_C. Even though large, thermally driven oscillation amplitudes of atoms in a liquid may hinder the establishment of a permanent long-range magnetic correlation at high temperatures, there is no rigorous argument against the occurrence of magnetic ordering in liquids.

The question arises whether it may be possible to find a "classical" metallic system showing magnetic long-range order in the liquid state. All magnetic elements and alloys have Curie temperatures far below the melting or liquidus temperature; but it is well established that metallic melts can be undercooled below their melting temperatures provided heterogeneous nucleation on container walls can be eliminated [3]. The alloy system exhibiting the smallest difference, $T_C - T_l$, between the Curie and liquidus temperatures is Co-Pd at the composition 80:20 [4]. This system offers the additional advantage that it is completely miscible. Confusion due to chemical clustering, as observed in, e.g., undercooled eutectic alloys [5] and its possible consequences on the magnetism of melts [6], can therefore be excluded [7]. By applying the electromagnetic levitation technique, $\mathrm{Co}_{80}\mathrm{Pd}_{20}$ can be undercooled by more than 300 K, i.e., 20 K below the Curie temperature of the solid phase, $T_C(s) = 1271$ K. Moreover, it can be kept for extended periods of time at such undercoolings [8], making direct measurements possible.

In the present work we report on quantitative measurements of the magnetization as a function of temperature in the undercooled melt regime of Co-Pd alloys of various compositions. The present experiments show a very pronounced Curie-Weiss behavior of the undercooled melt with transition temperatures from the paramagnetic to the ferromagnetic state slightly below $T_C(s)$. The Curie temperature of the magnetic undercooled melt $T_C(l)$ is determined.

The alloys of compositions $\mathrm{Co}_{100-x}\mathrm{Pd}_x$ $(x = 20, 25)$ were prepared from constituents of purity better than 99.99% by *in situ* melting in the levitation coil into spheres of about 6 mm diameter. Undercooling conditions were established in an electromagnetic levitation apparatus under high-purity environmental conditions. The sample is placed in a quartz tube surrounded by six water-cooled Cu windings and two counterwindings at the upper end of the coil which carry a radio frequency (260 kHz) current of maximum power of 4 kW. The temperature is measured remotely by a two-color pyrometer with an absolute accuracy of ±5 K. Before the experiment, the quartz tube is evacuated and then backfilled with a gas mixture consisting of 80 vol % He and 20 vol % H_2, providing a continuously cooling stream through the tube. The temperature of the sample is controlled by a proportional-integral-differential (PID) circuit in combination with an electromagnetic valve governing the gas stream and thus the heat transfer from the sample to the surrounding gas. This experimental setup allows high undercoolings owing to the avoidance of container wall-induced nucleation.

Undercooling is inferred from the respective temperature time profiles. The melting point is indicated by a discontinuous change of the slope at the solidus temperature T_s and the liquidus temperature T_l (1561 and 1606 K, respectively, for $\mathrm{Co}_{80}\mathrm{Pd}_{20}$ [9]). After melting and a moderate overheating, the melt cools and undercools. The crystallization sets in at the nucleation temperature T_n, at which the temperature of the undercooled melt starts to rise very rapidly owing to the release of the heat of fusion during crystallization (recalescence). The undercooling is determined as $\Delta T = T_l - T_n$.

The magnetization is measured with a Faraday balance, which was constructed such that it is compatible with the electromagnetic levitation technique. In brief, a small

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permanent magnet (CoSm) was fixed on one end of a torsion balance and placed in the vicinity of the coil while the sample was trapped in the rf field. At the sample position the strength of the magnetic field is 2×10^{-3} T and the field gradient amounts to 0.16 T/m. A small compensation coil was mounted very close to the permanent magnet. The magnet and compensation coil were shielded from the levitation coil by an aluminum plate. The electrical current through the compensation coil was adjusted such that the permanent magnet always stayed at the same position when the temperature of the sample was altered. An optical system consisting of a laser beam and a mirror permitted the control of the position of the magnet very accurately by adjusting the current through the compensation coil. The current I_M necessary to keep the magnet in its position is directly proportional to the variation of the magnetization (or susceptibility χ) with temperature: $I_M = C\,\Delta M \approx \chi$ (C is a calibration constant). Pure solid Co with well known χ [10] was used to calibrate the balance.

Figure 1 shows the current I_M of the compensation coil, normalized by the sample mass, as a function of the temperature of the liquid sample. A characteristic behavior of a ferromagnetic material is observed. During cooling from a temperature $T < T_l$, the signal rises very rapidly as the Curie temperature of the solid phase is approached. Measurements could be performed in the undercooling range $\Delta T = T_l - T_C \approx 340$ K. The rapid increase of the signal with increasing undercooling (or decreasing temperature) is throughout similar to that of the solid sample. The liquid state of the sample is unambiguously proven by the fact that after the measurement for each temperature the characteristic recalescence profile was clearly visible.

For a further analysis, the calibrated reciprocal signal l/χ is plotted versus temperature T for the liquid (solid circles) and the solid (crosses) sample (Fig. 2). In both cases linear behavior is observed indicating a Curie-Weiss-like relationship between the magnetization and temperature. The extrapolations of the data to $l/\chi = 0$ yields a Curie temperature for the solid of $T_C(s) = 1271 \pm 8$ K, in agreement with previous measurements [4], and a Curie temperature for the liquid of $T_C(l) = 1253 \pm 8$ K. These experiments clearly reveal a transition from the paramagnetic to the ferromagnetic state of long-range magnetic order in the undercooled melt.

The equal slopes of the two Curie-Weiss fits indicate a similarity of the magnetically ordered states of liquid and solid. Apparently the local moments of the magnetic ions are the same order of magnitude in the liquid and the solid state. This is reasonable because the densities of the face-centered-cubic structure of the solid and the dense-packed structure of the liquid differ by less than 4% [11]. It has been shown by Monte Carlo simulations [12] that in amorphous ferromagnets T_C is only slightly reduced by bond disorder (spatial fluctuations of exchange interactions due to the variations of nearest-neighbor distances). Assuming in a first approximation that a ferromagnetic liquid may be described from a magnetic point of view like an amorphous ferromagnet, we expect

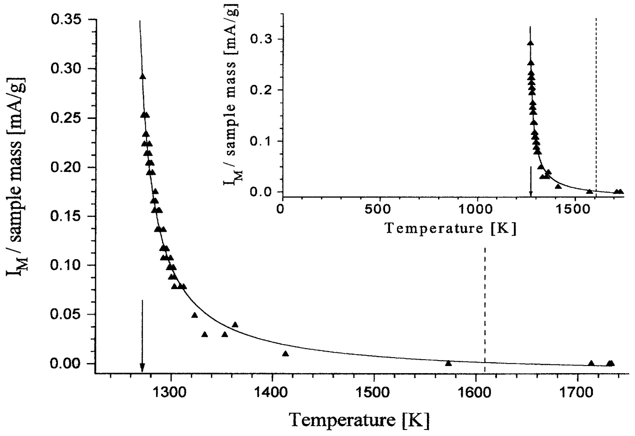

FIG. 1. Change of the magnetization, ΔM, as a function of temperature T in the undercooled liquid regime for $Co_{80}Pd_{20}$, measured with a modified Faraday balance. The data represent the measured values of I_M normalized by the sample mass, being proportional to ΔM. I_M is the current of the compensation coil needed to keep the permanent magnet in its position upon an alteration of the sample temperature. The dashed line marks the liquidus temperature, whereas the arrow indicates the Curie temperature of the solid magnetic phase. The solid line corresponds to a fit according to the Curie-Weiss law. The inset shows the magnetization over the entire temperature range.

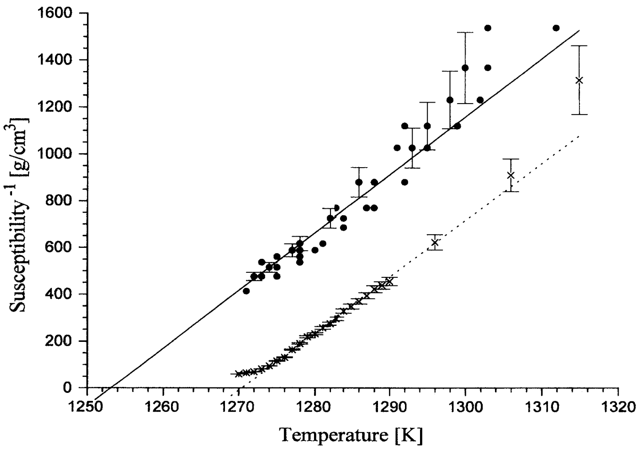

FIG. 2. The calibrated reciprocal susceptibility l/χ as a function of temperature. The symbols denote the results for the liquid undercooled sample (●) and the solid alloy (×). The two lines correspond to fits according to a Curie-Weiss law. The intersections at $l/\chi = 0$ are the Curie temperatures for the solid state, $T_C(s) = 1271 \pm 8$ K, and for the liquid state, $T_C(l) = 1253 \pm 8$ K.

that the bond disorder induced by melting the material has only a weak influence on lowering T_C.

In summary, a magnetic transition is detected in undercooled Co-Pd alloys and the Curie temperature $T_C(l)$ of the liquid state is determined. The existence of a transition from a paramagnetic to a ferromagnetic state of long-range order is supported by additional observations. First, at the Curie temperature both the solid and undercooled liquid samples started to vibrate strongly in the levitation coil because of the change in magnetic coupling with the rf field. Second, the dependence of the Curie temperature $T_C(l)$ on the composition of the Co-Pd alloys (not shown) is similar to that of the solid samples. Third, reference measurements on nonmagnetic samples, such as Al, do not show any interaction with the permanent magnet, whereas the deeply undercooled Co-Pd melt is attracted by a permanent magnet so strongly that it is displaced from the symmetry axis of the levitation coil [8]. Fourth, preliminary measurements of the specific heat as a function of temperature in the undercooled melt regime show a cusplike rise of the specific heat in the vicinity of the Curie temperature, being characteristic for a second-order phase transition such as the paramagnetic to ferromagnetic transformation. In contrast, measurements on the similar systems Pd-Fe and Pd-Ni show an almost constant specific heat since the smaller Curie temperatures of these alloys cannot be approached in undercooling experiments [13].

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