Magnetization of Ag Sinters Made of Compressed Particles of Submicron Grain Size and Their Coupling to Liquid ^{3}He

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The magnetic properties of sinters of compressed Ag particles of submicron grain size strongly deviate from the diamagnetic behavior of bulk Ag. Once exposed to a magnetic field, the sinters keep a permanent magnetic moment. Moreover, they exhibit an additional contribution to the magnetic moment which is independent of temperature in the investigated temperature range $5 \leq T \leq 300$ K. The possible origin of these anomalous magnetic properties and their relation to the magnetic field dependence of the thermal boundary resistance to liquid ^{3}He at millikelvin temperatures is discussed. [S0031-9007(98)06228-0]

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The thermal coupling between a metal and liquid ^{3}He at $10 < T < 100$ mK is well described by the acoustic mismatch theory of Khalatnikov [1] in which the energy exchange at the solid/liquid interface is attributed solely to phonons. This leads to a temperature dependence of the thermal boundary resistance $R_K \propto T^{-3}$ and results in a strong increase of the temperature difference at the interface towards lower temperatures. This phonon mediated coupling is not expected to exhibit a dependence on an applied magnetic field.

At temperatures below $\sim$10 mK, however, the observed boundary resistance between normal fluid ^{3}He and almost any metal clearly deviates from the T^{-3} behavior of the energy transfer due to phonons [2]. This deviation may be attributed to different origins.

(1) The cooling of liquid helium below $\sim$10 mK is achieved only by increasing the area for energy exchange using heat exchangers made of compressed metal particles with typical grain sizes ≤ 1 μm. Bulk phonons can propagate only through these sinters with wavelengths smaller than the dimensions of the particle which is fulfilled only at $T > 10$–20 mK [2]. However, long wavelength phonons should be able to propagate across the necks (interconnecting grain boundaries) of the compressed particles. These so-called soft phonons are expected to affect the temperature dependence of the boundary resistance [3].

(2) In addition to the heat transfer due to phonons (the *acoustic channel*) there is experimental evidence of a *magnetic channel* in the energy exchange at the ^{3}He/metal interface at $T < 10$ mK. Avenel *et al.* [4] observed that the boundary resistance between various bulk metals and liquid ^{3}He depends on the amount of magnetic impurities in the metal. Furthermore, the boundary resistance between metal sinters and liquid ^{3}He is strongly affected by an applied magnetic field. This field dependence, in turn, significantly depends on the sinter material; whereas Perry *et al.* [5] report a *decrease* of R_K with increasing magnetic field for a platinum sinter, Osheroff and Richardson [6] observe an *increase* of R_K with increasing field and a saturation at $B > 0.2$ T for a silver sinter.

The existence of a magnetic contribution to the boundary resistance and the quest for its origin is a long-standing problem. Perry *et al.* [5] interpret their results as a weak magnetic coupling of conduction electrons to the localized nuclear moments of a solid ^{3}He layer at the *platinum* metal surface. In contrast, Osheroff and Richardson [6] point out that this mechanism does not explain their results for the coupling between *silver* sinter and liquid ^{3}He. They emphasize the influence of surface oxygen in its various magnetic forms on the magnetic coupling. Theoretical investigations show that neither dipolar nor short-ranged exchange interactions between the spins of liquid ^{3}He and of conduction electrons in metals are strong enough to make an observable contribution to R_K [7]. Based on the results of Ref. [6], Nakayama separated the observed thermal resistances into two independent paths of magnetic and nonmagnetic contributions [8]. However, the resulting nonmagnetic boundary resistance still clearly deviates from the bulk value of the acoustic mismatch theory; this discrepancy might then be explained in terms of low-lying vibrational modes of the Ag sinters [8]. Clearly, the mechanisms of the heat transfer at the liquid/solid interface are not yet fully understood.

We report a different approach to obtain information on the magnetic channel of the heat transfer between liquid ^{3}He and a metal sinter by studying the magnetic properties of the sinter itself. We have chosen Ag sinters made of particles with submicron grain size [9] as this particular material is commonly used in low temperature experiments for the study of liquid and solid helium. The sinter samples from powders with nominal grain sizes of 40 and 70 nm were compressed at about 4 kbar to form small cylinders ($\phi = 5$ mm, $l \sim 3$–5 mm, $M \sim 0.2$–0.5 g). Brunauer, Emmett, and Teller (BET) measurements [10] resulted in

specific surface areas of ≈ 1.5 m^2/g for both powders thus indicating that the actual grain size $d_{Ag} \approx 400$ nm which is consistent with the observation of other authors [11]. In order to be able to further distinguish between both powders, however, we refer to their nominal grain sizes throughout the paper.

Measurements were performed in a SQUID magnetometer [12] at $1.5 \leq T \leq 300$ K and in magnetic fields $0 \leq B \leq 6$ T. A mass spectroscopy analysis of the powders provided as an average concentration of magnetic impurities (for both grain sizes): Fe $\simeq$ 10 ppm, Mn, Co, and Ni < 0.5 ppm. We found a large content of Mo in the powders (40 nm: 0.1%; 70 nm: 0.01%–0.25%) which is consistent with the analysis of Ref. [6] for their Ag sinter.

Our data demonstrate that the magnetic properties of the Ag sinters strongly deviate from those of bulk Ag. Measurements of the magnetization of two bulk Ag samples were performed and confirmed the magnetic properties expected for the bulk material. Figures 1(a) and 1(b) show the field dependence of the magnetic moment

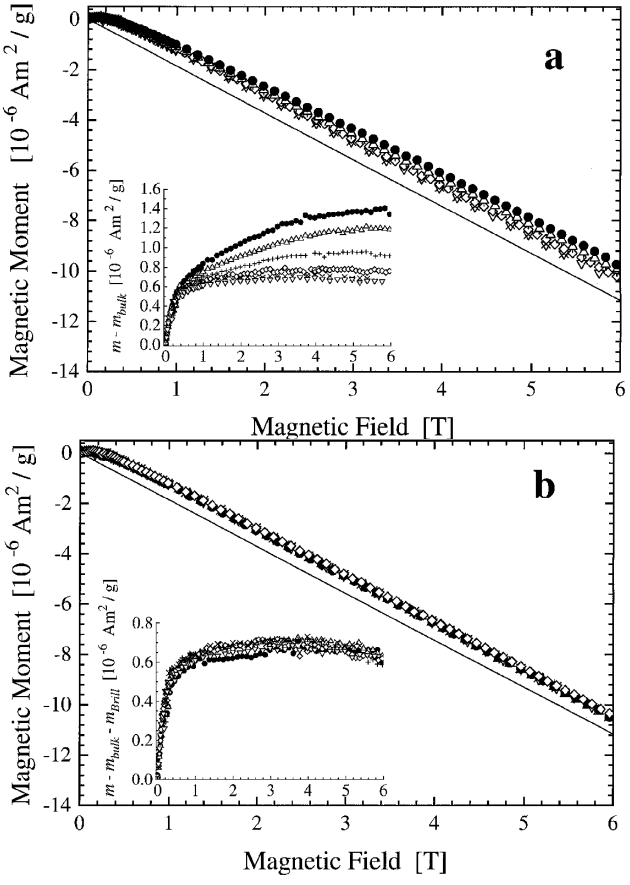

FIG. 1. (a) Field dependence of the magnetic moment of a 40 nm Ag sinter at: (•) 5 K, (△) 10 K, (+) 20 K, (◇) 50 K, (×) 100 K, (▽) 300 K. Inset: Data after subtraction of the bulk Ag moment. (b) Data of (a) corrected for the contribution of localized paramagnetic impurities. Inset: Data after subtraction of the bulk Ag moment. The solid lines represent the data measured for bulk Ag.

m of a sinter made of 40 nm Ag powder; a similar behavior is observed for the 70 nm sinters too, although the magnitude of the effects is smaller in the 70 nm samples. Surprisingly, at $B < 0.3$ T, the measured magnetic moment is almost independent of the applied magnetic field. Only at $B > 0.3$ T is the diamagnetic behavior expected for bulk Ag observed. However, the absolute value of the magnetic moment is clearly decreased compared to the data of bulk Ag. The *temperature* dependence of the magnetic moment in Fig. 1(a) at a constant field reflects the contribution of localized paramagnetic moments described by the Brillouin function; the inset in Fig. 1(a) shows the data after subtraction of the magnetic moment of bulk Ag in order to make this temperature dependence more transparent. The correction of the data for the localized moments (according to a fit of the Brillouin function to the data of the T dependence at constant field) removes this apparent temperature dependence and causes all data to fall on a single curve [Fig. 1(b)]. The anomalous field dependence at low fields, however, remains unaffected. The subtraction of the diamagnetism of bulk Ag from the sinter data presented in Fig. 1(b) reveals the field dependence of an additional contribution to the magnetization of the sinters [inset of Fig. 1(b)] which will be discussed in more detail below. The susceptibility of the Ag sinters obtained from the field dependence of their magnetic moment at fields $B > 1$ T [Fig. 1(b)] is given by $\chi = -0.18$ μemu/g which compares well to the value reported in the literature for bulk Ag ($\chi = -0.19$ μemu/g) [13].

Thermal treatment of the sinters significantly alters their magnetic properties towards bulk behavior [14] as during the annealing process more and more particles are melting together. This leads to a clear reduction of the surface area too, from ≈ 1.5 m^2/g before annealing to a value which is almost the bulk surface value of the sample of ≈ 2.5 cm^2/g. We observe that the anomalous magnetic properties of the Ag sinters vanish when the samples are exposed to temperatures close to the melting temperature of Ag ($T_M = 1235$ K) for almost four days. After this long term heat treatment only a slight deviation of the magnetic properties of the sinters from the bulk behavior remains.

Apart from the Langevin paramagnetism of the localized magnetic impurities and the diamagnetism of the Ag matrix, there is a *temperature independent* contribution to the magnetic moment of the Ag sinter with a distinct magnetic field dependence: it first strongly increases with increasing field until it starts to saturate at ~ 0.3 T and remains constant up to $B = 6$ T [see inset of Fig. 1(b) and Fig. 2]. This field dependence of the additional contribution to the magnetic moment resembles the B dependence of the *permanent* magnetic moments which the sinters surprisingly keep after exposure to a magnetic field (inset of Fig. 2 and Ref. [15]). Moreover, there is a strong similarity of the field dependence of this unexpected contribution

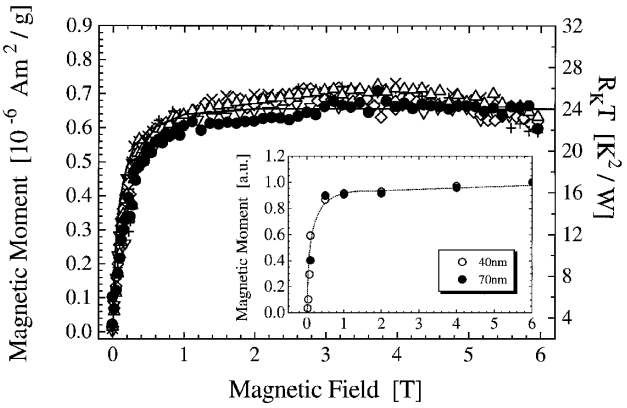

FIG. 2. Left axis: B dependence of the additional magnetic moment of a 40 nm Ag sinter [see inset of Fig. 1(b)]. The symbols are the same as in Figs. 1(a) and 1(b). Right axis: The solid line represents the data of Ref. [6] for the thermal boundary resistance between an Ag sinter and liquid ^{3}He. Inset: Dependence of the permanent magnetic moment (at $T = 10$ K, normalized to $B = 6$ T) of a 40 and a 70 nm sinter on the magnetic field the sample was exposed to before the permanent moment was measured (in zero field) [15]. The dotted line is only a guide for the eye.

with that of the thermal boundary resistance between normal fluid ^{3}He and an Ag sinter measured by Osheroff and Richardson [6]. The solid line in Fig. 2 represents their smoothed data of R_K taken at $T \approx 1$ mK. This striking agreement in the field dependence of both sets of data indicates that the magnetic coupling of liquid ^{3}He to the Ag sinter seems to be related to the anomalous magnetic properties of the Ag sinter.

Osheroff and Richardson [6] suggested as a main source for the observed B dependence of R_K adsorbed oxygen on the large surface of the sinter. However, we do not observe any change in the magnetic moment of the sinters at $\approx 20 \leq T \leq 45$ K, where different magnetic phase transitions of oxygen should be clearly detectable [16]. Localized paramagnetic impurities may be ruled out as a possible origin, too, as the data shown in Fig. 2 are already corrected for paramagnetic contributions from randomly distributed single impurity moments. However, this correction does not account for any magnetically ordered moments in the sinter. One might interpret the field dependence of the additional contribution (Fig. 2) as well as the existence of a permanent magnetic moment as an indication for the presence of a magnetically ordered subsystem in the sinter. In the following we will discuss two properties of the permanent magnetic moment of the sinters which support this idea.

If the anomalous magnetic properties of the sinters are caused by magnetically ordered impurities, the study of the influence of thermal treatment on the permanent magnetic moment could provide indications for a possible ordering temperature. We have generated a permanent moment in the sinters in $B = 6$ T at $T = 10$ K; subsequently, the samples were annealed at various temperatures up to 1100 K for 30 minutes. After each annealing step, their permanent moments were measured in zero field. Figure 3 shows the decrease of the permanent moments with increasing temperature; at $T \sim 800$ K their values are beyond the resolution of our magnetometer. This temperature is remarkably close to the Curie temperature T_c of magnetite (Fe_3O_4; $T_c = 860$ K [17]). A further observation on the permanent moment may be interpreted as an even stronger indication for the presence of Fe_3O_4 in the sinters: this is the step in the T dependence of the permanent magnetic moment at $T \simeq 120$ K which is only weakly observable for the 70 nm samples but which is much more pronounced for the 40 nm sinters (inset of Fig. 3 and Ref. [15]). At $T \simeq 120$ K, a structural phase transition occurs in Fe_3O_4 (electronic ordering of Fe^{2+} and Fe^{3+} ions on the B sites of the lattice) which is the cause of the observed metal-insulator transition in Fe_3O_4 [17]. The step in the T dependence of the permanent magnetic moment of the sinters might be attributed to this so-called Verwey transition in magnetite [18]. The magnetization of an Ag sinter mixed with a small amount of Fe_3O_4 powder shows a strongly enhanced signal at

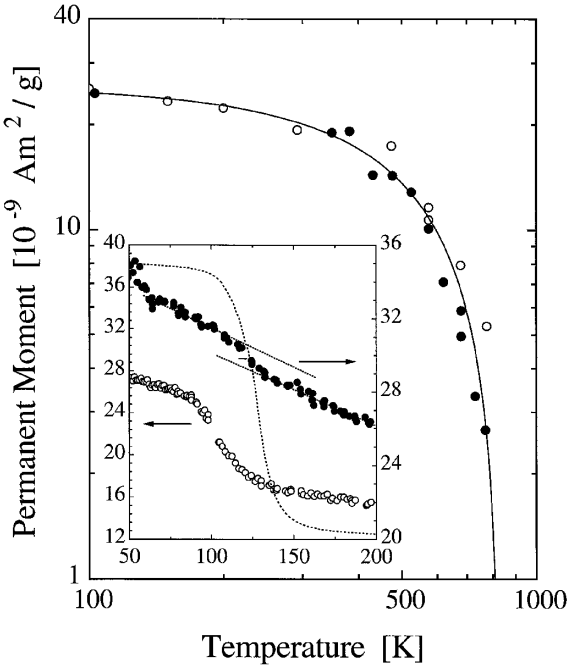

FIG. 3. The permanent moments of the 40 (∘) and the 70 nm (•) sinters that decrease with increasing temperature. The solid line is a fit to the data. Inset: The left (right) axis corresponds to the permanent moment of a sinter made of a 40 (∘) [70 nm (•)] powder in the as-received state. The dashed line represents smoothed data of the permanent moment of a 40 nm sinter mixed with Fe_3O_4 powder (mass ratio $M_{Ag}/M_{\text{oxide}} \approx 400{:}1$; for this sample, the scale of the y axis has to be multiplied by a factor of ≈200). The only weakly observable transition in the 70 nm samples might be explained by a smaller amount of Fe_3O_4 in this powder.

the transition at $T \simeq 120$ K compared to the sinters made from the as-received powders. Finally, even the large Mo content in the Ag sinters might contribute to their magnetic properties as the spinel Fe_2MoO_4 shows a weak ferromagnetism below ~400 K [19].

For a discussion of a possible mechanism which relates the magnetic properties of the Ag sinters to their thermal boundary resistance to liquid ^{3}He, we assume just one ferromagnetically ordered Fe_3O_4 grain per Ag particle ($d_{Ag} \simeq 400$ nm) which results in a grain of a size of ≈10 nm. The magnetic moment μ of such a ferromagnetic grain can be estimated to be $\approx 20\,000\mu_B$ using μ (Fe_3O_4 molecule) $= 4.1\mu_B$ [17]. Obviously, the Zeeman splitting in mT fields of these grains does not result in energies of the order of $E/k_B \sim$ mK necessary for the energy transfer between the liquid and the particles. However, a broadening of the Zeeman levels due to dipole-dipole interaction [$k_BT \simeq (\mu_0/4\pi)(\mu^2/r_{NN}^3)$ for nearest neighbors] similar to the effect discussed by Osheroff and Richardson for oxygen at the surface [6] may well be of the order of some mK $\times$ k_B and, therefore provide a possible mechanism for the energy transfer. The suppression of the magnetic channel by applying magnetic fields of the order of a few tens of milliteslas can then be understood as the effect of increasing the energy gap between the broadened Zeeman levels well above k_BT.

To summarize, the magnetic properties of sinters of submicron Ag particles deviate strongly from the diamagnetic behavior of bulk Ag: we observe an additional contribution to the magnetic moment which is temperature independent at least at $5 \leq T \leq 300$ K. There are strong indications that this additional moment might be caused by magnetically ordered impurities in the sinter. Its distinct magnetic field dependence agrees well with the B dependence observed for the thermal boundary resistance between liquid ^{3}He and an Ag sinter of the same grain size. We conclude that the magnetic channel for the heat transfer at the liquid/solid interface is mainly governed by a magnetically ordered subsystem, and that the magnetic coupling is determined by only a few ppm of the whole sinter material. Preliminary results of the study of the magnetic properties of Ag sinters made of a different submicron powder [20] reveal significantly less magnetically ordered impurities in this powder. Zero field boundary resistance measurements between this sinter and normal fluid ^{3}He show much larger values for R_K at $T \approx 1$ mK [21] compared with the Ulvac sinters; this supports our conclusion that magnetically ordered impurities play an important role for the magnetic channel of the energy transfer. More systematic studies of the dependence of the magnetic properties of the sinters, in particular, on the concentration of magnetic impurities, should not only lead to an explanation for the results presented above, they should finally provide a possibility to control the magnetic channel for R_K. Moreover, our results clearly indicate that any study of magnetic properties of liquid and solid helium in the environment of an Ag sinter may be significantly affected by the magnetic behavior of the sinter.

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