

Reduced Susceptibility of Irradiated Palladium

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The ac susceptibility of thin PdFe films has been measured before and after low-temperature irradiation with inert noble gases by using a newly developed susceptometer. The disorder introduced by the irradiation causes a reduction in both the Curie temperature by a factor of 2 and the Curie constant by a factor of about 7. From this result it is calculated that the low-temperature irradiation reduces the susceptibility of the Pd host by more than an order of magnitude, thus explaining the recently observed superconductivity in irradiated Pd.

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Palladium is a metal with very interesting properties, especially in regard to its potential for being a superconductor. From its high electronic density of states at the Fermi surface, $N(0)$, and its reasonable phonon spectrum one would expect a rather large electron-phonon coupling, and thus a reasonably high superconducting transition temperature. However, superconductivity has not been observed down to 1.7 mK.¹ The reason is that Pd has a large Stoner enhancement factor of $[1 - UN(0)]^{-1} \approx 10$,² where U is the exchange parameter. The resulting spin fluctuations are sufficient to explain the absence of superconductivity.

However, recent experiments showed that Pd can be transformed into a superconductor with a T_c of about 3 K by the introduction of lattice disorder via low-temperature irradiation with He⁺ ions.³ This result agrees qualitatively with the theoretical predictions for superconductivity in Pd without spin fluctuation.^{4,5} Therefore it was suggested that the disorder reduces $N(0)$, which is large and strongly peaked in crystalline Pd, and correspondingly the spin fluctuations are diminished. This would result in a decrease of $N(0)$ and thus in a reduction of the susceptibility of Pd after low-temperature irradiation. The aim of the experiment described in the following was to test these assumptions for the occurrence of superconductivity by measuring the ac susceptibility before and after irradiation.

In the following we report measurements of the ac susceptibility of crystalline and irradiated thin PdFe films which were used instead of pure Pd to investigate the above suggested variations of the Pd properties. The magnetic Fe atoms serve as a probe of the magnetic behavior of the Pd host matrix itself. Thus, one of the major difficulties of this experiment, i.e., the small available volume (due to the limited sample thick-

ness ~ 1000 Å which can be reached by the irradiated ion beam) and the correspondingly small susceptibility signal, could be overcome. The exchange enhancement of the Pd matrix of PdFe alloys at fairly small Fe concentrations creates ferromagnetic ordering of so-called "giant moments." Via long-range conduction-electron polarization, the Fe moments induce a small moment on a cloud of neighboring Pd atoms.⁶ The resulting giant moment is very large $[(10-12)\mu_B \text{ per Fe}]$ and ferromagnetism persists down to low concentrations (≥ 0.1 at. % Fe). The magnetic susceptibility of dilute PdFe alloys follows a Curie-Weiss law⁷ in the paramagnetic regime at $T \leq 20$ K, where χ_0 is almost independent of temperature:

$$\chi = \chi_0 + C/(T - \theta_C), \quad (1)$$

where χ_0 is the susceptibility of Pd without magnetic Fe atoms. From the changes of the paramagnetic Curie temperature, θ_C , and the Curie constant, C , after irradiation of the PdFe alloy, the change of the exchange-enhanced susceptibility χ_0 of the pure-Pd host can be calculated.

For the measurement of the susceptibility of the PdFe films an ac-induction apparatus (Fig. 1) similar to the design described by Hilsch, Korn, and Minnigerde⁸ has been attached to the Jülich 400-keV ion accelerator.

The film is magnetized by a homogeneous ac magnetic field (1170 Hz, 0.39 mT) parallel to its surface. Two astatic flat pickup coils are wound behind the sapphire substrate parallel to the sample and to the ac driving field. The stray field from the magnetized film penetrates both coils symmetrically giving rise to a doubled amplitude of the signal. For a fixed temperature the resulting signal can be compensated to zero.

The important feature of this susceptometer, which allows the measurement of susceptibility

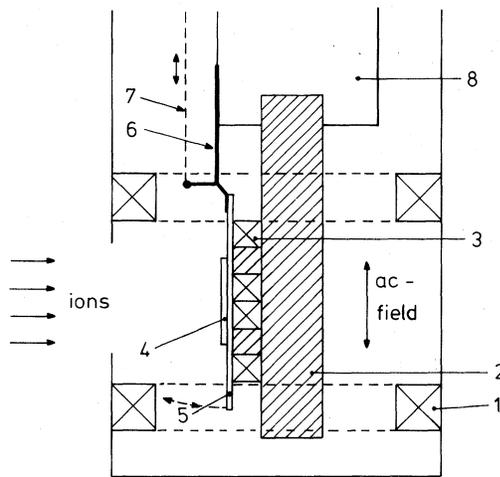


FIG. 1. Ac susceptometer attached to the 450-keV Jülich accelerator: (1) field coils, (2) sapphire holder, (3) pickup coils wound parallel to the ac field, (4) PdFe film, (5) sapphire substrate, (6) plastic spring, (7) nylon thread moving the film toward and away from the pickup coils, and (8) Cu support.

changes before and after irradiation, is the possibility to measure the signal of the astatic coils with and without a sample. Thus it is possible to determine absolute voltage changes with a resolution ≈ 1 nV. The sample is moved toward and away from the pickup coils by means of a nylon thread. The movement is done in such a way that the sample is alternately 30 sec away from and close to the pickup coils. In the latter position, which is also used during the irradiation, the restoring force of a plastic spring ensures good thermal contact between the sapphire substrate of the evaporated film and the sapphire support of the pickup coils.

Pure-Pd films⁹ of ~ 500 Å thickness are prepared at room temperature by electron-beam evaporation at $\sim 10^{-8}$ Torr with rates of 25 Å/sec onto 0.2-mm-thick sapphire substrates. The Pd-coated area of the substrate is 6×15 mm². The PdFe alloy is produced by implanting 1.31×10^{15} /cm² Fe⁺ ions into the pure-Pd films at temperatures below 20 K. The implantation energy of 100 keV corresponds to a projected range $R_p \approx 260$ Å with a width of the implanted Gaussian profile of $2\Delta R_p \approx 280$ Å.¹⁰ From this implanted profile the content of Fe atoms in the peak of the distribution is calculated to be 0.55 at.%. The inhomogeneous distribution of the Fe atoms in the Pd host is homogenized by irradiation with Ar⁺ ions at room temperature and vacuum anneal-

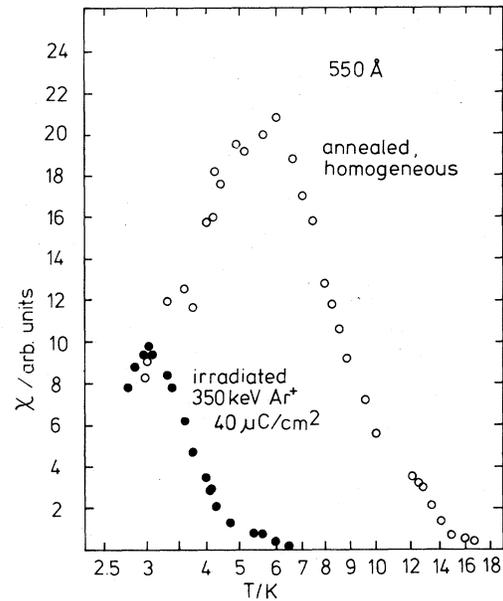


FIG. 2. The temperature dependence of the low-field (0.39 mT) ac magnetic susceptibility for Pd (0.35 at. % Fe). The open circles are for the annealed film. The closed circles represent the susceptibility for the same film after low-temperature Ar⁺ irradiation.

ing at 50 °C for two days. The resulting Fe concentration amounts to 0.35 at.%. The Fe homogeneity was confirmed by a depth analysis with secondary ion mass spectroscopy (SIMS) to be within $\pm 15\%$.

Figure 2 shows the susceptibility as a function of temperature (open circles), in arbitrary units, of a 550-Å Pd film with 0.35 at. % Fe "homogeneously" distributed. The observed Curie temperature of about 6 K agrees fairly well with the value of about 6.7 K in crystalline bulk PdFe.¹¹ After this measurement, the PdFe film is irradiated at low temperatures with only 2.5×10^{14} Ar⁺ ions/cm² at a flux of 10^{11} cm⁻² sec⁻¹ and an energy of 350 keV. This energy corresponds to a projected range of $R_p \approx 1100$ Å.¹⁰ Therefore, nearly all ions penetrate through the 550-Å Pd film causing only lattice defects within it. The closed circles in Fig. 2 show the susceptibility of this irradiated PdFe film. Obviously the introduced disorder significantly reduced the Curie temperature as well as the Curie constant. This result was not changed with increasing Ar⁺ fluence.

Annealing the irradiated PdFe film at room temperature (30 °C) restored the susceptibility of the sample to that measured before irradiation (open circles).

In the investigated temperature range below 20 K the relatively small susceptibility χ_0 of the Pd host can be neglected. (The increase of χ is of the order of 10^3 for PdFe.) From the inverse susceptibility $1/\chi$ as a function of temperature the paramagnetic Curie temperature θ_C of the annealed PdFe film is determined to be 6.9 K, whereas the irradiated film shows a θ_C of 3.4 K. The ratio of the Curie constants of the annealed film and the irradiated film is calculated to be 7.9. The determination of θ_C from the Curie behavior is difficult because of the width of the ferromagnetic transition. The transition is presumably broadened by statistical concentration fluctuations of the Fe atoms in Pd.⁶ For this reason the temperature at the sharp peak in the susceptibility curves of Fig. 2 is useful as the lower limit of the Curie temperature. For the annealed film 6 K is observed in contrast to 3 K for the irradiated one. By defining these temperatures as Curie temperatures, a ratio of the Curie constants of the annealed and the irradiated film can be calculated to be 6.8 from the experiment. Thus the mean ratio of the Curie temperatures is 2 and the mean ratio of the Curie constants is about 7.

In order to evaluate the present data on PdFe we considered it a rough but very useful approximation to apply a molecular mean-field theory for giant-moment alloys.⁷ Both the Fe concentration and the external fields are small and the temperature is sufficiently low. Whereas the susceptibility of PdFe is given by Eq. (1), the paramagnetic Curie temperature is described by

$$\theta_C = N_{Fe} g^2 \mu_B^2 S(S+1) \alpha^2 \chi_0 / 3k_B \quad (2)$$

and the Curie constant is given by

$$C = N_{Fe} g^2 \mu_B^2 S(S+1) (1 + \alpha \chi_0)^2, \quad (3)$$

where N_{Fe} is the number of magnetic Fe ions and α describes the interaction between the conduction electrons and the localized Fe moment. S is the magnetic quantum number of the Fe ions. The magnitude of the effective giant moments leading to ferromagnetism in PdFe is given by^{7,12}

$$\mu_{eff} = \mu_{Fe} (1 + \alpha \chi_0), \quad (4)$$

where μ_{Fe} is the moment of Fe, which is about $3\mu_B$.⁶ For low concentrations the giant moment per Fe atom is of the order of $(10-12)\mu_B$ in PdFe.⁶

In the following we want to compare the annealed (subscript a) with the irradiated (subscript i) properties of the PdFe film. For the ratio of the

Curie constants we find

$$\frac{C_a}{C_i} = \left(\frac{1 + \alpha_a \chi_{0a}}{1 + \alpha_i \chi_{0i}} \right)^2 \approx 7 \quad (5)$$

because in (3) all constants besides $\alpha \chi_0$ do not depend on irradiation. From Eqs. (4) and (5) it can be concluded that the effective giant moment in irradiated Pd (0.35 at. % Fe) is reduced by a factor of 2.7. From Eq. (4) we find $\alpha_i \chi_{0i} = 0.5$ or 0.2 and $\alpha_a \chi_{0a} = 3$ or 2.2 with $12\mu_B$ or $10\mu_B$ assumed for the giant moment in the annealed PdFe.

From Eqs. (2) and (4) we obtain

$$\left(\frac{\alpha_a}{\alpha_i} \right)^2 \frac{\chi_{0a}}{\chi_{0i}} = \frac{\theta_a}{\theta_i} = 2,$$

demonstrating a remarkable decrease of the susceptibility caused by the irradiation:

$$\frac{\chi_{0i}}{\chi_{0a}} = \frac{1}{2} \left(\frac{\alpha_i \chi_{0i}}{\alpha_a \chi_{0a}} \right)^2 \approx 0.04.$$

We have shown that the susceptibility of low-temperature irradiated Pd is strongly reduced in comparison to the annealed metal. From this result we can conclude that the Stoner enhancement factor in annealed Pd is substantially reduced by the irradiation. The harmful spin fluctuations are diminished and superconductivity in irradiated pure Pd becomes possible.

The present results for the susceptibility of Pd are in good agreement with earlier suggestions to explain the superconductivity. Whereas the calculated electronic band structure of crystalline Pd (Refs. 13 and 14) reveals that the Fermi energy is located in a narrow peak of $N(E)$ it was argued that irradiation substantially reduces $N(0)$. There are mainly two reasons for this reduction: (i) smearing of the band structure due to disorder and (ii) change of the local symmetry of Pd atoms due to Pd interstitials. The reduction of $N(0)$ results in a reduction of the Stoner enhancement factor and hence superconductivity may become possible in a Pd film without spin fluctuations.

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Anisotropy-Triad Dynamics in Spin-Glasses

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In Heisenberg spin-glasses, the orientation of a state is specified by a reference spin triad $(\hat{n}, \hat{p}, \hat{q})$, and its anisotropy is specified by a rotation ψ of this state away from its equilibrium orientation. Rotation of $(\hat{n}, \hat{p}, \hat{q})$ by $-\psi$ defines an *anisotropy triad* $(\hat{N}, \hat{P}, \hat{Q})$, whose dynamics is derived. This dynamics is exclusively dissipative, consistent with torque and ESR measurements. Analogy to ordinary glasses suggests a Vogel-Fulcher law for the associated relaxation time.

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A valuable picture of the spin-glass (SG) state has emerged from the numerical simulations of Walker and Walstedt for a prototype SG, CuMn .¹ These authors randomly substitute Mn atoms for Cu, and study the local energy minima for a Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling. They find that, in each local minimum, the Mn spins point in all three spin directions, in a fashion that overall would appear random to the eye. Individual spin orientations are thus specified with respect to an orthonormal triad, which I call the *spin triad* $(\hat{n}, \hat{p}, \hat{q})$.² The orientation of the state as a whole is given by specifying $(\hat{n}, \hat{p}, \hat{q})$, where \hat{n} is taken along the remanent magnetization \vec{m}_0 ; the orientation of \hat{p} and \hat{q} (about \hat{n}), however, cannot be associated with any macroscopic observable.

Because the anisotropy energy of real SG's is found to be independent of the magnitude $m_0 \equiv |\vec{m}_0|$, SG anisotropy has been somewhat puzzling.^{3,4} Indeed, Schultz *et al.*,⁴ who successfully interpreted a large part of their ESR data in terms of a uniaxial anisotropy involving $\hat{n} \cdot \hat{N}$,

comment that " \hat{N} is a fixed (in space) direction whose origin remains a mystery to us." Even more mysterious is the fact that torque experiments show, under certain circumstances, that the anisotropy axis \hat{N} is *not* fixed, but rotates with respect to the crystal.^{5,6}

If anisotropy in SG's were specified only by rotations about axes which are normal to \hat{N} , it would be the purpose of this paper to derive the dynamics of \hat{N} . However, the microscopic calculations of Fert, Levy, and Morgan-Pond⁷ have shown that an anisotropy torque develops on rotating an equilibrium SG state about *any* axis $\hat{\psi}$. This torque is along $\hat{\psi}$, and its magnitude (as well as the anisotropy energy) depends only on the magnitude ψ of the rotation angle. $\vec{\psi} \equiv \psi \hat{\psi}$ gives the relative orientation between the apparent lattice orientation (as given by the density matrix which specifies the state) and the actual lattice orientation (as given by the Hamiltonian). Although it is sufficient to specify the anisotropy by $\vec{\psi}$, as in Ref. 7, for the present purposes it is more convenient to work with $(\hat{n}, \hat{p}, \hat{q})$ and a gen-