Ferromagnetism of Pd-Fe alloys produced by low-temperature ion implantation

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We present low-field magnetization measurements on Pd-Fe films and foils obtained by low-temperature implantation of 175-keV Fe^+ ions into pure Pd. dc magnetization measurements are performed *in situ* with a superconducting quantum-interference device magnetometer. The Curie temperatures T_C of the implanted films and foils are significantly lower than the bulk values. We demonstrate that the decrease of T_C is due to defects produced during implantation. Two effects are observed, an increase in the critical concentration x_c for ferromagnetism and a decrease in dT_C/dx_{Fe}, the rate of change of T_C with the Fe concentration x_{Fe}. Employing annealing experiments, preirradiation of Pd films and foils with Ar^+ and He^+ and preimplantation of O^+, we demonstrate that changes in x_c are due to oxygen-stabilized defects, whereas changes in dT_C/dx_{Fe} are due to vacancies, interstitials, and small defect clusters.

I. INTRODUCTION

Low-temperature ion implantation and irradiation have become a very successful tool in obtaining metastable materials with new electronic properties.[1] In some instances, the damage produced by low-temperature implantation and/or irradiation can significantly change the electronic properties of a given metal or alloy. Thus, it was shown that the radiation damage produced by He^+ irradiation of thin Pd films near 10 K can completely change their properties: from a large exchange-enhanced paramagnet in the undamaged state to a superconductor at high defect concentrations.[2] Later it was shown that Ar^+ irradiation of a weakly ferromagentic Pd-Fe film causes a decrease in its Curie temperature.[3] It was argued that this decrease is a result of a decrease in the exchange-enhanced susceptibility of Pd due to the presence of defects.[3] At a sufficiently high defect concentration the paramagnetism of the Pd matrix can be completely destroyed, leading to the observed superconductivity in the highly irradiated Pd films.[3]

In a different experiment it was shown that the Curie temperature of sputtered Pd-Fe films is significantly lower than the corresponding bulk value.[4] It is very likely that this difference is, at least in part, also due to the presence of defects in the sputtered films. Thus it is evident that defects can significantly alter the electronic properties of Pd and Pd-Fe alloys. However, very little is known about the nature of these defects and the mechanism responsible for the observed changes. In this paper we present the first systematic study of the effect of radiation damage produced at liquid-He temperatures on the magnetic properties of weakly ferromagnetic $Pd_{1-x}Fe_x$ alloys. Particular emphasis is placed on the difference in behavior of thin films and thick foils, and on the effect of oxygen. Some of our results were already published previously.[5]

II. EXPERIMENTAL METHODS

A. Sample preparation

All Pd-Fe alloys for the magnetization measurements were obtained by Fe^+ implantation into pure Pd. Two types of samples were prepared. For one, the starting material was a 75-nm-thick Pd film on a separate substrate. The evaporation was carried out in a ultrahigh-vacuum (UHV) electron-beam evaporator onto sapphire substrates previously outgassed at 700 °C. The other type of sample was obtained from 0.025-mm-thick Pd foils mounted with vacuum grease on sapphire substrates similar to the ones used for the films. The dimensions of the sapphire substrate are $1\times5\times50$ mm^3, and the area of the Pd sample attached to the lower end of the sapphire was 5×30 mm^2. For the films, we used Pd from Johnson Mathy (Puratronic, 99.997% purity), and for the foils we used Pd from Ventron (99.9% purity). The sapphire substrates with either the Pd film or foil were mounted into the cryostat for ion-implantation and *in situ* magnetization measurements.[6]

To obtain Pd-Fe alloys at various Fe concentrations, Fe^+ ions were implanted into the Pd films and foils with a previously described implantation machine.[7] During the implantation the sample was kept at temperatures lower than 20 K. After the desired level of implantation was reached the sample was lowered *in situ* into the pick-up coils of a S.H.E. Corporation superconducting quantum-interference device (SQUID) probe for magnetization measurements.[6] Then, the sample could be repositioned for continued implantation.

The $^{56}Fe^+$-ion implantation was performed at a fixed energy of 175 keV and at ion currents of 0.2—0.3 μA as measured at the sample. A typical Fe-concentration profile and radiation-damage profile for 10^{16} Fe^+/cm^2 implanted at 175 keV into Pd films or foils is shown in Fig.

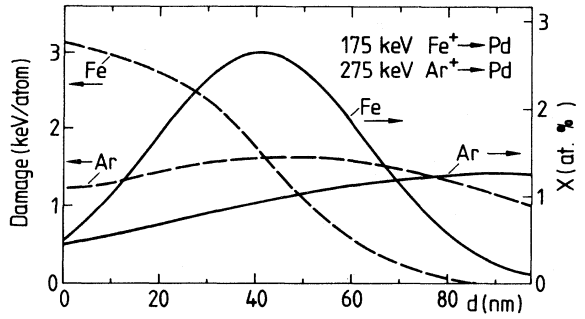

FIG. 1. Calculated Fe and Ar concentration profiles after implantation of 10^{16} Fe^+ (Ar^+) ions/cm^2 into Pd (solid lines, right-hand scale). The dashed lines (left-hand scale) show the corresponding damage profile produced by the Fe^+ (Ar^+) implantation. The calculations are based on a program by D. K. Brice (Ref. 8).

1. The profiles were obtained with the help of a computer program by Brice.[8] The maximum of the Gaussian concentration profile is at about 40 nm beneath the surface of the films or foils. In Fig. 1, Ar^+-concentration and associated damage profiles for irradiation experiments with 275-keV Ar^+ ions, discussed below, are also shown. The absolute value of concentrations is accurate only within 20%,[8] while relative concentration changes can be determined within 1%.[1]

B. Magnetization measurements

The main purpose of the magnetization measurements was to determine the onset of ferromagnetic order in the implanted samples. This can be done most conveniently by measuring the dc magnetization in a very small magnetic field as a function of temperature. Typically, fields of 0.1 or 0.2 G were trapped inside the superconducting Nb shield.[6] The lowest temperature reached was 1.1 K. Figure 2 shows one example of the measured magnetization of an implanted film and foil. Displayed is the magnetization measured with a S.H.E. Corporation flux counter[6] in arbitrary units as function of temperature. The indicated Fe concentration is the maximum of the Gaussian profile. The sudden onset of the magnetization signals the appearance of ferromagnetic order in the center of the implanted region. The continued steep increase in the magnetization with decreasing temperature (field cooling) is, in part, due to the concentration profile. With decreasing temperature the ferromagnetic order grows from the center of the profile to include a larger and larger volume of the implanted layer. However, this increase in the magnetization is also due to the relatively strong hysteretic behavior of the samples. The behavior is demonstrated in Fig. 2. It shows the magnetization obtained after initially cooling in zero field ($<10^{-2}$ G) to the lowest temperature of 1.1 K, and then measuring the magnetization in 0.1 G with increasing temperature. The zero-field-cooled and field-cooled branches meet at a temperature where the hysteresis disappears, which, in these types of alloys, is equal to the Curie temperature. This hysteresis leads to a peak in the ac susceptibility exactly at T_C, as observed for implanted Pd-Fe (Ref. 3) and also several bulk alloys.[9] For the implanted film, this temperature is the highest Curie temperature corresponding to the maximum in the construction profile. In the remainder of this paper we use the extrapolation of the fairly linear field-cooled branch to the temperature axis (see Fig. 2) as the value for T_C corresponding to the maximum of the profile. This value is well defined and agrees with the temperature at which the two branches meet (Fig. 2).

To demonstrate the effect of the hysteresis on the magnetization, we measured the field-cooled and zero-field-cooled magnetization of a bulk Pd-Fe sample. The sample had been severely deformed to produce enough dislocations for domain-wall pinning. In this state it displayed a sharp peak in its ac susceptibility at its Curie temperature of $T_C=10$ K.[10,11] Figure 3 displays the two branches of the magnetization for this sample. Again the field-cooled branch continues to increase below T_C. The

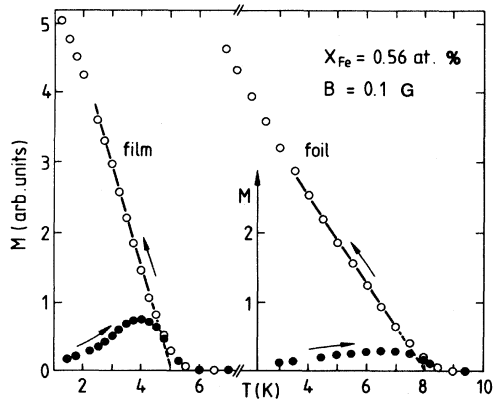

FIG. 2. Magnetization vs temperature after low-temperature implantation of 0.56 at. % Fe into a Pd film ($T_C=5$ K) and a Pd foil ($T_C=8$ K). The closed circles give the results for zero-field-cooling measurements, and the open circles show the corresponding field-cooling behavior. The straight lines are used to define T_C by extrapolation.

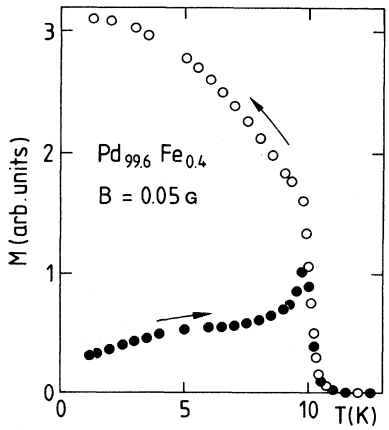

FIG. 3. Magnetization vs temperature for a Pd-Fe bulk sample. The closed circles show the zero-field-cooling behavior, and the open circles show the field-cooling behavior.

two branches meet exactly at T_C. The similarity of Figs. 2 and 3 demonstrates that the concentration profile does not qualitatively alter the magnetization curves; it also justifies the method chosen to obtain T_C for the implanted samples.

It is obvious from Fig. 2 that there is no qualitative difference between foils and films. We only measure the temperature-dependent part of the magnetization. Thus, for a thick foil, the weakly temperature-dependent paramagnetic signal of the bulk of the Pd foil is not affected by implantation and does not contribute to our signal. Any difference between film and foil is due to a difference in radiation damage. Thus, our T_C measurement is a unique way to investigate ion implantation in thick foils where only a small region beneath the surface is affected.[5]

III. RESULTS AND DISCUSSION

A. Concentration dependence of T_C

Figure 4 displays a typical set of magnetization measurements for a 75-nm-thick Pd film implanted with Fe^+ to various concentration levels. The concentrations given are those of the maximum of each concentration profile. During the complete set of measurements and implantation steps the sample was always kept below 30 K. For each concentration the Curie temperature T_C determined by extrapolation as described above is well defined. The corresponding measurements on the thick foil look qualitatively the same (see Fig. 2).

Curie temperatures determined from the magnetization measurements are displayed in Fig. 5. Shown is the T_C for foils, and as well as for films, as a function of the maximum concentrations in the various profiles. The pluses are for oxygen-doped foils and will be discussed below. Also shown for comparison are T_C values for bulk Pd-Fe alloys.[12] There is a considerable scatter in the T_C values reported in Ref. 12. New low-field measurements on two very homogeneous Pd alloys[11] are also shown in Fig. 5. These new values are consistent with the lower values reported in Ref. 12. For clarity, only those lowest

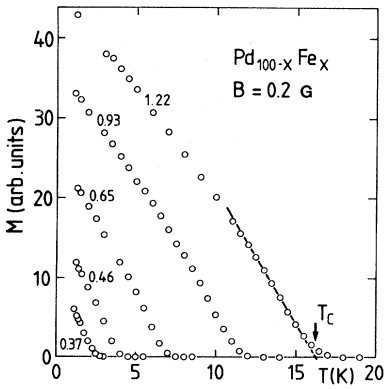

FIG. 4. Magnetization vs temperature for several implanted Pd-Fe films; numbers labeling the curves are the maximum Fe concentrations of the implanted profile in units of at. %. The straight line shows how T_C was determined by extrapolation.

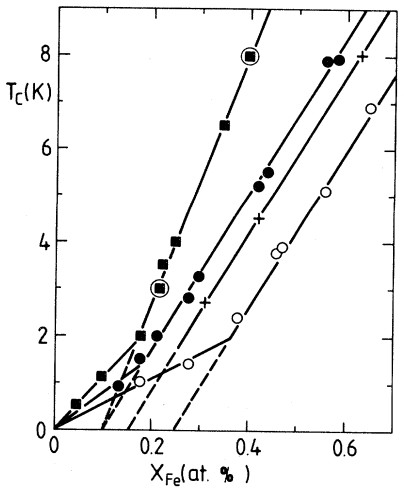

FIG. 5. Curie temperature T_C vs Fe concentration x_{Fe} of Pd-Fe bulk alloys (■), implanted foils (●), and implanted films ○. The symbols (◙) represent new, unpublished data of bulk alloys (see Ref. 11). The pluses denote data for Pd foils predoped with 1500 ppm oxygen.

T_C values are displayed in Fig. 5. The higher T_C values reported in Ref. 12 could be due to several factors, namely inhomogeneity, extrapolation from excessively high magnetic fields, and oxygen impurities.[11]

The general shape of the T_C-vs-x_{Fe} curves is the same as that observed in other alloys.[9,13] The extrapolation of the steep part yields the critical concentration x_c for ferromagnetism.[9,13] The change in slope of T_C vs x_{Fe} at low concentrations is, as in many other alloys, probably due to a change-over to spin-glass ordering.[9,13] The T_C values of foils and films in Fig. 5 are each results from two independent implantation sequences such as the one shown in Fig. 4. Thus, our relative concentrations are quite accurate. The fact that x_c for the implanted foil is the same as that for the bulk (0.10 at.% Fe; see Fig. 5) is indicative of the fact that our absolute concentrations are much better than the possible 20 % (see Sec. II A above).

The effect of implantation on T_C can be summarized in the following way: The T_C values of the implanted films and foils are all significantly lower than the bulk values (Fig. 5). Two effects are observed: first, a change in the slope dT_C/dx_{Fe} from 27 K/at. % for the bulk to 16 K/at. % for implanted films and foils alike; second, an increase in the critical concentration to $x_c = 0.25$ at. % for the films from $x_c = 0.1$ at. % for bulk and implanted foils. We will demonstrate below that these changes in T_C are due to radiation damage produced during implantation, and that the two effects, namely the changes in x_c and dT_C/dx_{Fe}, are due to different types of defects.

B. Annealing experiments

To investigate the annealing of radiation-induced defects, several samples were heated to various temperatures. After each annealing, T_C was remeasured. For temperatures above 50 °C, the samples had to be removed from the cryostat and sealed in a quartz capsule. This procedure was very time consuming and only a few experiments of

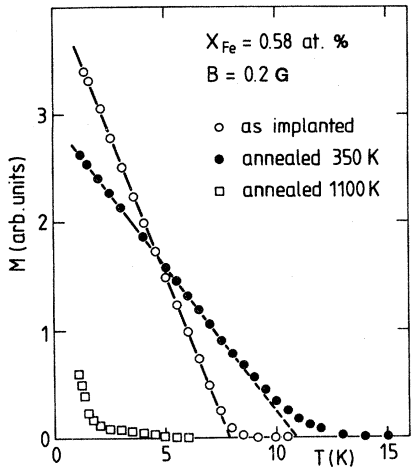

FIG. 6. Magnetization vs temperature for a 0.58-at. % Pd-Fe foil after different annealing temperatures: ○, as implanted at $T < 20$ K; ●, annealed at 350 K; and □, annealed at 1100 K.

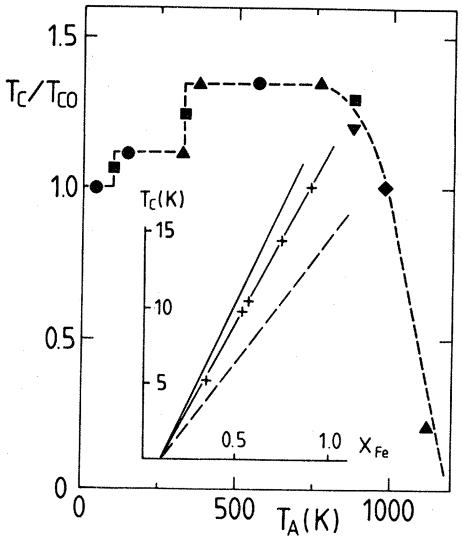

FIG. 7. Curie temperature T_C normalized to its value after low-temperature implantation T_{C0} vs annealing temperature T_A. Each symbol represents a different sample of implanted Pd foils. The dashed line is only a guide for the eye. Inset: pluses are the Curie temperatures of foils after annealing at about 500 K; solid and dashed lines represent T_C values of bulk samples and as-implanted foils, respectively.

this kind were performed. Figure 6 shows a typical set of magnetization curves of an implanted foil after annealing at various temperatures. The annealing times vary between 15 min at the highest temperatures to several hours at the lowest. Also shown in Fig. 6 is the magnetization curve for the state directly after implantation. Annealing at 350 K increases T_C considerably. Annealing at 800 K (not shown) yields the same T_C as the 350-K state. However, annealing at an even higher temperature of 1100 K dramatically decreases T_C. Two other annealing sequences on different foils yielded similar results. A surprising feature of the measurements in Fig. 6 is the decrease in signal strength on annealing. We will discuss this effect in Sec. III H below.

All annealing experiments on foils are summarized in Fig. 7. It displays the Curie temperature of different foils (different symbols) as function of the annealing temperature T_A. For display purposes the T_C values are normalized to the as-implanted value T_{C0}. The dashed line is just a guide for the eye. The first two annealing steps seen in Fig. 7 are in agreement with earlier experiments on neutron-irradiated pure Pd. There, interstitials and vacancies were observed to anneal at 40 and 350 K, respectively,[14] A third increase in T_C, signaling the annealing dislocations, is absent in Fig. 7. Instead, T_C decreases dramatically at higher annealing temperatures. Direct measurement of the Fe-concentration profile by secondary-ion mass spectroscopy (SIMS) revealed that this sharp decrease in T_C is caused by a significant broadening of the profile.[15] The maximum of the profile had decreased from 0.58 to about 0.2 at. % Fe.[15]

The inset of Fig. 7 compares the T_C values of foils annealed between 350 and 800 K (maximum T_C values) to those of bulk and as-implanted foils. x_c is still at 0.10 at. %; however, the dT_C/dx_{Fe} value has increased to 23 K/at. % (from 16 K/at. % just after implantation), but is still short of the bulk value of 27 K/at. %. The remaining difference may be due to extended defects such as dislocations not yet annealed.

The one annealing experiment performed with an implanted film is consistent with the above results. It shows that at the same concentration, both film and foil reach the same T_C after annealing at around 500 °C. Thus, it seems that the smaller T_C values of implanted films (see Fig. 5) are due to a large concentration of defects.

This difference in defect concentration between thick foils and thin films has been observed before.[16,17] It is thought to be due to the relatively high disorder and/or impurities in the starting Pd films.[16,17] One could speculate at this point that the increase in x_c observed for the films is due to this initial disorder in films. This could be checked immediately by producing a higher concentration of defects in the starting materials by Ar^+ irradiation.

C. Preirradiation with Ar^+

For this sequence of experiments we irradiated the pure-Pd films and foils with 275-keV Ar^+ ions, again at temperatures below 20 K. These damaged films and foils were then directly implanted with Fe^+ ions to investigate the effect of Ar^+-irradiation damage on T_C. At 275 keV, most Ar^+ ions end up either in the substrate of the films or deep inside the foils. There is strong evidence that the Ar atoms located in the Fe region have no direct effect on the electronic properties of the films and foils[17] (see also Sec. III F below).

For the irradiation experiments, Ar^+ fluences of up to 3×10^{16} ions/cm^2 were used. Figure 8 displays the results of the effect of Ar^+ preirradiation on T_C. For comparison, the T_C values of the Fe-implanted samples from Fig. 5 are also shown as the two solid lines. In both films and foils the preirradiation of Ar^+ increases x_c. For the foil, an Ar^+ fluence of 10^{16} Ar ions/cm^2 increases x_c from 0.10 to 0.2 at. % Fe (Fig. 8, solid squares). Similarly, Ar^+

preirradiation of Pd films with the same Ar^+ fluence increases x_c from 0.25 to 0.35 at. % Fe (Fig. 8, open triangles). Continued Ar irradiation in the Fe-doped films still causes a considerable decrease in T_C (a shift in x_c). The open circles and squares in Fig. 8 were obtained after an Ar^+ irradiation of Fe-doped films with a total fluence of 2×10^{16} and 3×10^{16} ions/cm^2, respectively. After the Ar^+ irradiation, the Fe implantation was continued. For the determination of the maximum of the Fe-concentration profile we took into account the sputtering caused by the high Ar irradiation.[18,19] There is no indication of any saturation behavior of the decrease in T_C caused by irradiation of Pd films by Ar^+. A very different behavior is seen in foils. There, subsequent Ar^+ irradiation of the samples represented by solid squares in Fig. 8 has hardly any effect on T_C. Thus, we conclude that, in contrast to films, the damage produced by Ar^+ preirradiation of thick foils saturates at about 10^{16} Ar ions/cm^2. This value is about 2 orders of magnitude larger than what is typically observed to lead to a saturation concentration of defects such as interstitials, vacancies, or small defect clusters by low-temperature irradiation of foils with heavy ions of several hundred keV.[20] A clue to how this discrepancy can be resolved comes from experiments where thin films were irradiated with heavy ions up to high fluences ($\phi > 10^{15}$ ions/cm^2). Here, for simple metals such as In or Al (Refs. 17 and 21) and transition metals such as Mo or V,[22,23] clear evidence could be provided that oxygen impurities, inevitably present within films due to the preparation process, are able to stabilize radiation damage. In detail, by using thin-film targets with different amounts of oxygen, it could be demonstrated[21] that the ion fluences needed to produce a noticeable concentration of oxygen-stabilized defects depend on the oxygen concentration c_O of the films: The lower c_O, the higher the ion fluences needed to produce oxygen-stabilized defects. In all of the above examples, the relatively pure films ($c_O < 1$ at. %), heavy-ion fluences of the order 10^{16} ions/cm^2 were necessary to produce a significant amount of these oxygen-stabilized defects. This compares well with the fluence found to be necessary to give a clear shift of the critical Fe concentration x_c in Ar^+-preirradiated Pd foils and films. Thus, it is tempting to assume that this type of defect is produced by Ar^+ irradiation of Pd foils with high fluences.

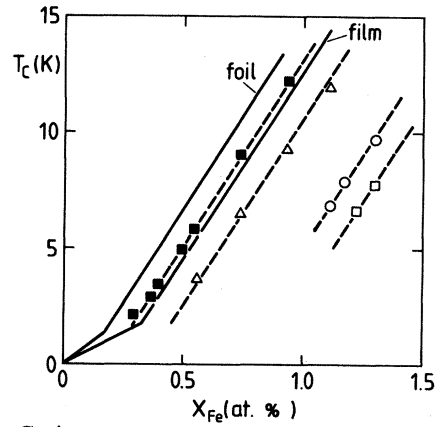

FIG. 8. Curie temperature T_C vs Fe concentration x_{Fe} for different samples irradiated at $T < 20$ K with 275-keV Ar^+ ions prior to Fe implantation. Open symbols denote Pd films, and closed symbols denote Pd foils. ■ and △, preirradiated with 10^6 Ar ions/cm^2; ○, irradiated with 2×10^{16} Ar ions/cm^2; and □, irradiated with 3×10^{16} Ar ions/cm^2. For comparison, the solid lines give the results of the Fe implantation into Pd foils and films.

For foils, the formation of oxygen-stabilized defects implies the presence of these impurities within the starting Pd sample. In films, on the other hand, oxygen impurities can be transported into the sample by secondary irradiation effects. Here, collisional mixing at the substrate/film interface plays a crucial role, particularly in irradiation experiments, where the ions pass through the film into the substrate and their nuclear stopping power at the substrate/film interface is rather high. In order to have collisional mixing on a scale larger than 10 nm, high fluences are necessary, again of the order of 10^{16} ions/cm^2.[24] Thus in films, in addition to the commonly much higher oxygen concentration as compared to foils, the substrate can act as an impurity source via collisional mixing, if high irradiation fluences are used. With this process in mind, and assuming for the moment that oxygen-stabilized defects result in a shift of the critical Fe concentration x_c to higher values, the results shown in Fig. 8 can be explained qualitatively in the following way.

Even in "pure" Pd foils a small amount of oxygen is present (in the following subsection this oxygen concentration is estimated to be $c_O \sim 300$ ppm). Owing to this small c_O value, high Ar fluences are necessary to produce a noticeable concentration of oxygen-stabilized defects. Eventually, since it is reasonable to assume that the stabilization ability of each oxygen atom can be saturated, a maximum concentration of stabilized defects is approached. This is reflected by the saturation behavior of x_c, the property affected by this type of defects. In films, on the other hand, oxygen atoms can be transported from the sapphire substrate into the sample during the irradiation by the above-described mixing process. This readily explains, in Pd films as opposed to foils, why no saturation behavior of the x_c shifts is observed with increasing Ar fluence. As mentioned previously, films are expected to contain higher oxygen concentrations than foils. Thus in films, equal Ar^+ fluences should lead to a higher concentration of stabilized defects than in foils. Correspondingly, the x_c shift is expected to be larger in films than in foils, as observed experimentally (Fig. 8). In addition, for a film sample, the production of oxygen-stabilized defects, as monitored by a corresponding x_c shift, should be observable at a fluence lower than that for a foil. This explains the observed difference of the x_c values found for Fe-implanted Pd foils and films. In films the oxygen concentration is sufficiently high so that the collision processes due to the implanted Fe atoms can result in stabilized defects, leading to an x_c increase above the bulk value. In Pd foils with a much lower oxygen concentration than in films, the Fe fluences used for implantation are not sufficient to produce a noticeable amount of stabilized defects, (quantitatively, the Fe fluence necessary to obtain

$x_{Fe}=0.1$ at. % is $\phi_{Fe}=4\times10^{14}$ ions/cm^2, i.e., this fluence is small compared to the Ar fluence of $\phi_{Ar}=10^{16}$ ions/cm^2). Thus, in foils, x_c is not affected by the Fe implantation and agrees with the bulk value. An obvious test of this hypothesis is to increase the oxygen content of the Pd foil prior to Fe implantation.

D. Implantation of oxygen

To increase the oxygen content of a Pd foil we first implanted 100-keV O^+ ions, giving rise to an oxygen profile with a maximum of 1500 ppm oxygen 40 nm beneath the surface. Subsequent Fe implantation into this oxygen-doped foil yielded the T_C values shown as crosses in Fig. 5. A clear shift in x_c from 0.10 to about 0.15 at. % Fe is observed. A simple linear extrapolation to the film results would yield an oxygen concentration of about 4000 ppm, not an unreasonable amount for a film. Furthermore, scaling the observed change in x_c to the total fluence of the Ar^+-preirradiation results of Fig. 8, and that of the oxygen results of Fig. 5, yield an oxygen content of about 300 ppm for pure-Pd foil, a value quite possible for the solubility of oxygen in Pd.[11,25]

E. Radiation damage and magnetism in Pd-Fe

How could one qualitatively understand the observed effects of radiation damage on the magnetic properties of Pd-Fe? Pd-Fe is a so-called giant-moment ferromagnet.[12,13] In the dilute limit each Fe atom polarizes the surrounding exchange-enhanced Pd matrix to form a large polarization cloud with a total moment of about $10\mu_B$.[26] At 0.1 at. % Fe these clouds reach their percolation threshold for long-range ferromagnetism.[12,26]

The effect of radiation damage on the magnetic properties of Pd-Fe alloys is not yet understood in any microscopic way. However, it is quite plausible that defects can cause a significant change in local electronic properties, and thus may directly affect the formation of polarization clouds. We propose the following qualitative picture.

We know from our experiments that defects reduce the magnetization of Pd-Fe alloys. It is also known that in foils at relatively low fluences, such as those reached in our direct Fe-implantation experiments, defects such as vacancies and interstitials are produced at a concentration of about 1000 ppm.[17,20]

These defects are responsible for the observed decrease in dT_C/dx_{Fe} in the Fe-implanted foils. Near the percolation threshold of 0.1 at. % Fe, we have, on the average, about one defect per polarization cloud. Thus, it is likely that the reduction of T_C occurs via a reduction of the exchange enhancement of the Pd susceptibility near a defect, and a simultaneous reduction of the local polarization cloud. At the moment we are not able to give any estimates about the magnitude of this effect.[27]

The other effect of radiation defects, namely the increase in the critical concentration, is due to oxygen-stabilized defects as shown above. It appears that some Fe atoms are completely neutralized by these defect complexes and do not participate in the ferromagnetic order, thus increasing x_c. It is possible that near one of these defects the Pd susceptibility is completely reduced. Any Fe atom near this defect does not produce a polarization cloud and thus has little effect on T_C.

Mössbauer experiments on sputtered Pd-Fe films with very low T_C values reveal a low-field component in the effective-field distribution.[4] Is it possible that these low effective fields come from Fe atoms near oxygen-stabilized defects? In the remainder of the paper we present additional experiments to support our interpretations.

F. Irradiation of annealed samples

To ensure that the changes of T_C observed during the annealing experiments (see Fig. 7) are indeed due to the annealing of defects, we irradiated the annealed samples with 275-keV Ar^+ ions. This irradiation should produce the same defects as before annealing. Figure 1 shows an example of the damage produced and the local Ar concentration after a fluence of 10^{16} Ar ions/cm^2. There is previous evidence that the Ar atoms remaining inside the films has little effect on the electronic properties[21] (see also He irradiation below). Figure 9 displays the effect of the Ar irradiation on the T_C of Pd-Fe films and foils. Several films and foils were irradiated. For display purposes, the T_C values are normalized to the value in the annealed state before irradiation.

As expected for foils, the radiation damage saturates at a fluence of about 10^{14} ions/cm^2. At the relatively small fluences used for Fig. 9, oxygen-stabilized defects are not yet observed (see above). In contrast to the behavior of foils, no saturation is observed in films. Also, the initial decrease in T_C is significantly larger than that observed in foils. This is consistent with the relatively large amount of oxygen present inside the films (see above). The absence of any saturation is due to the above-mentioned mixing effect at the substrate interface. Also shown in Fig. 9 is the result obtained in Ref. 3 by low-temperature Ar irradiation after prolonged ion-beam mixing at room temperature. The result would be consistent with ours if we assume that the ion-beam mixing increased the oxygen level to almost 1 at. %.

We also performed irradiation experiments of annealed

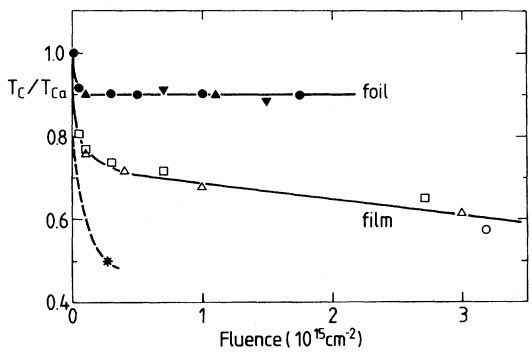

FIG. 9. Curie temperature T_C normalized to its value after annealing at 500 K, T_{Ca}, vs Ar^+ fluence. Each symbol represents a different sample; the asterisk represents a result from Ref. 3.

Pd-Fe foils with 175-keV He^+ ions. The T_C changes are identical to those after Ar^+ irradiation (Fig. 9). At 175 keV, the range of He^+ is 500 nm,[8] i.e., essentially all He atoms end up deep inside the foil, well beyond the ferromagnetic region. The identical effect on T_C of He and Ar irradiation again confirms that implanted Ar atoms do not directly affect the electronic properties of Pd (see also Sec. III C above). It also makes it difficult to understand why superconductivity in Pd films is observed only after He^+ irradiation, but not after Ar^+ irradiation.[2]

G. Effect of the Fe profile on T_C

To investigate the influence of the Fe profile on our method to determine T_C we implanted Fe at various energies into one foil. Figure 10 shows Fe-concentration profiles calculated[8] after implanting Fe at energies between 100 and 275 keV. The curve labeled 1 corresponds to a 275-keV implantation. The other curves are obtained after additional Fe implantations at successively lower energies. Figure 11 shows the Curie temperature for this sample as function of the concentration-profile maximum. The solid line represents the T_C values for the 175-keV Fe implantation in foils (Fig. 5). The error bars indicate the uncertainty in the extrapolation of the magnetization curves. The inset shows the magnetization at 0.2 G as a function of temperature for the concentration profile labeled 3 of Fig. 10. Owing to the asymmetric profile these curves are no longer as simple as in the earlier experiments. However, within these errors and the error in the calculation of the profiles,[8] the highest Curie temperature determined by our extrapolation is indeed determined by the maximum of the profile and not by any of its other features.

H. Temperature dependence of the magnetization

In Secs. II B and III B we already mentioned that the continued increase of the magnetization M below the Curie temperature T_C is largely due to hysteresis and not due to the Fe profile. In a simple ferromagnet, M in low fields reaches a limiting value (reciprocal demagnetization factor multiplied by applied magnetic field) at T_C and remains equal to this value below T_C.[9] The constancy of M is caused by the spontaneous formation of domains exactly compensating the increase in spontaneous magnetization below T_C.[9] However, if the sample displays significant anisotropy and hysteresis below T_C, the formation

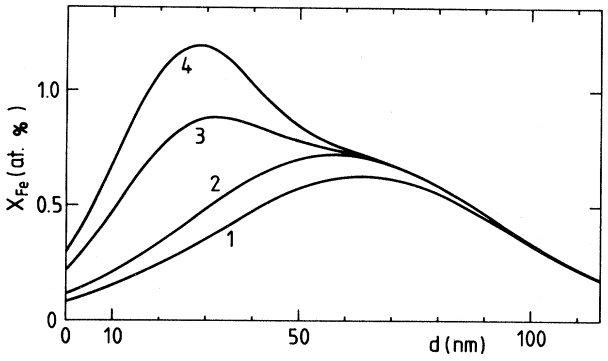

FIG. 10. Concentration profiles of Fe implanted into Pd, calculated by superposition of different Gaussian profiles corresponding to different implantation energies (275, 175, and 100 keV).

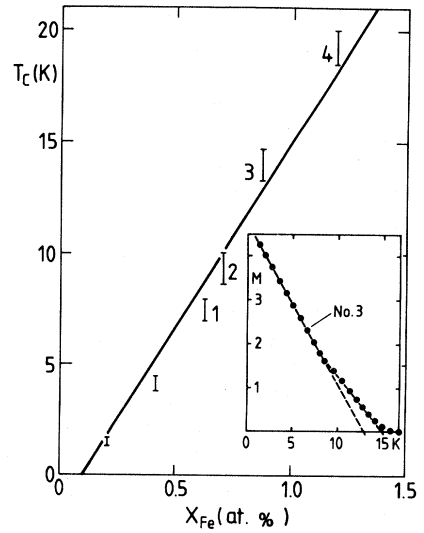

FIG. 11. Curie temperature vs Fe concentration for a Pd foil. The number labeling the transition temperatures correspond to the concentration profiles from Fig. 10. The solid line gives the results for a Fe^+-implantation energy of 175 keV (from Fig. 5). Inset: Magnetization vs temperature for sample 3 of Fig. 10, demonstrating the difficulty to define T_C due to the profile asymmetry.

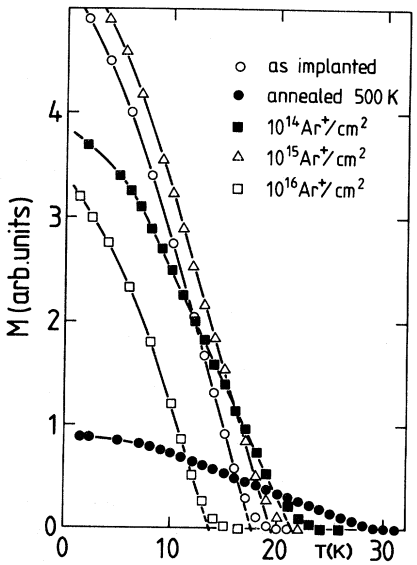

FIG. 12. Magnetization vs temperature for a Pd film containing 1.30 at.% Fe—○, as-implanted at $T<20$ K; ●, annealed at 500 K. The annealed sample is then irradiated at $T<20$ K with 275-keV Ar^+ ions with different fluences: ■, 10^{14} Ar ions/cm^2; △, 10^{15} Ar ions/cm^2; and □, 10^{16} Ar ions/cm^2.

of domain walls may be prevented, leading to the magnetization curves as shown in Figs. 2 and 3. Well-annealed bulk Pd-Fe alloys do not display any significant hysteresis below T_C.[11] The hysteresis necessary to explain the behavior of implanted films and foils (Fig. 2) is probably due to the defects produced by implantation. Annealing should largely eliminate the defects and thus the hysteresis, and as a consequence M should increase much less below T_C. Figure 12 displays exactly such a behavior of an implanted Pd-Fe film. The open circles were obtained directly after Fe implantation. Annealing at 500 K (solid circles) increases T_C from 17.6 to 29 K. However, M increases much less below T_C. The remaining increase of M below T_C in this annealed state may be solely due to the Fe profile. Creation of defects after annealing should again produce hysteresis and a large increase in M below T_C. This is also demonstrated in Fig. 12 by a sequence of Ar irradiations after annealing. As the defect concentration increases, T_C decreases but the M-vs-T curves become steeper.

IV. SUMMARY

We have demonstrated that the ferromagnetic Curie temperature T_C is a sensitive probe for radiation defects. Measurements were performed on samples produced by low-temperature implantation of Fe^+ ions into Pd films and foils. The nonuniformity of the Fe concentration (Gaussian profile) did not complicate the T_C determination. Comparison of the T_C-vs-x_{Fe} curve to that of the bulk alloys revealed a considerable decrease in T_C of Fe-implanted films and foils. This decrease was shown to be due to defects produced by the implantation process. These defects were observed to anneal at temperatures typical of interstitials and vacancies in Pd. Additional measurements, consisting of preirradiation of Pd films and foils by Ar^+ and He^+, preimplantation of oxygen, and irradiation of annealed Pd-Fe films and foils, identified two distinct effects of the radiation-induced defects. First, the increase in the critical concentration for ferromagnetism in films and foils is due to the neutralization of Fe moments by oxygen-stabilized defects. Second, the decrease of the rate of which T_C changes with x_{Fe} is due to simple defects such as vacancies and interstitials which locally reduce the Pd susceptibility and cause a decrease in the polarization-cloud moment.

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[27]In Ref. 3 the reduction in the Pd susceptibility by irradiation was estimated to be about a factor of 7. However, by comparing the width of the ferromagnetic transition measured in Ref. 3 to new bulk measurements (see Ref. 11 and also Fig. 3), it is quite obvious that the sample in Ref. 3 is rather inhomogeneous. It is not very meaningful to fit Curie-Weiss law to a smeared-out ferromagnetic transition; thus the factor of 7 is not a valid estimate.