implies that the distribution $g(\Delta)$ is a general property of the glasses and that the spread of activation energies is a result of disorder. Finally, the results confirm the prediction of the valence-alternation model that defects similar to those in semiconducting chalcogenide glasses would also be present in oxides.

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Superconductivity in Irradiated Palladium

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Pure palladium films, evaporated between 4.2 and 300 K, can be transformed into superconductors by means of irradiation at low temperatures with He^+ ions. The maximum transition temperature obtained is 3.2 K. It is shown that the presence of a special kind of defects produced during the irradiation is a necessary precondition for the occurrence of superconductivity.

Palladium represents the most strongly exchange-enhanced material among the pure metals. It has a Stoner enhancement factor[1] of $1/[1 - UN(0)] \approx 10$, where U is the exchange parameter and $N(0)$ the electron density of states at the Fermi surface. The occurrence of such strong spin fluctuations is thought to be the reason for the absence of superconductivity[1] above 2 mK.[2] Theoretical calculations[3-5] show that Pd without spin fluctuations should be a superconductor. The calculated values for the corresponding superconducting transition temperatures, T_c, vary between 0.3 (Ref. 5) and 7 K (Ref. 3).

In the present paper it will be shown that Pd

becomes a superconductor as a result of irradiation with He^+ ions at low temperatures. Furthermore, the results show that a special kind of disorder, introduced by low-temperature irradiation, is necessary for the occurrence of superconductivity in Pd. The maximum T_c obtained is 3.2 K,[6] in good agreement with the predictions for Pd without spin fluctuations. A possible explanation will be given for the reduction of spin fluctuations during low-temperature irradiation. The possibility of a "*p*-wave" pairing mechanism[7] in Pd can be excluded in these experiments because of the large number of lattice defects introduced by the irradiation.

The irradiation experiments at low temperatures were performed in a modified ^3He-^4He dilution refrigerator attached to the Jülich 400-kV ion accelerator. The resistance of the sample can be measured after irradiation down to 0.1 K with a standard four-point-probe technique. The temperature of the Pd itself remained below 8 K during the maximum flux of the He^+ beam, $\Phi = 3 \times 10^{12}$ cm^{-2} sec^{-1}, at an energy of 130 keV. The energy of the He^+ ions corresponds to a projected range $R_p = 3500$ Å in Pd with a standard deviation $\Delta R_p = 750$ Å.[8] Since the purpose of the irradiation is only to damage the Pd we use evaporated Pd films with thicknesses $\lesssim 1000$ Å in order to avoid He atoms sticking inside Pd. In the case of a 1000-Å (200-Å, respectively) Pd film only 4×10^{-4} (5×10^{-6}) of the total amount of He^+ ions stay inside the Pd.

Great care was taken to ensure the purity of the evaporated Pd films. The starting material (99.999+% Pd, Johnson-Matthey) contained 5 ppm Ru and 6 ppm Pt as main impurities but only 1.5 ppm Fe and 0.8 ppm Ni. The Pd films have been evaporated either *in situ* onto a substrate at 4.2 K, or in an UHV chamber onto substrates at 150–300 K. In order to check for any dependence of the occurrence of superconductivity on the evaporation conditions the latter were varied over a wide range as indicated in Table I. The analysis of a nonoptimal Pd film (10^{-8} Torr, 3 Å/sec, 200 K) by Auger-electron spectroscopy revealed no detectable N, O, and S impurities (detection limits 0.5, 0.25, and 1.0%). All investigated Pd films, independent of the special details during evaporation, showed the following common properties:

(i) All as-condensed films stay normal to the lowest measured temperature of 0.2 K.

(ii) All films become superconducting after He^+ irradiation at low temperatures. From this we conclude that superconductivity is really a property of the irradiated Pd itself and is not induced by impurities.

Only under the following conditions it was possible to produce Pd films which did not become superconducting after the irradiation procedure:

(1) Evaporation pressure: 8×10^{-6} Torr. This experiment shows that gaseous impurities are not helpful for superconductivity in Pd. In addition, implantations of C and N into Pd foils lead to T_c values of only 1.2 and <0.2 K, respectively.[9]

(2) Annealing of a Pd film to 500 K for four hours in 3×10^{-10} Torr before irradiation. This result is in agreement with further observations, that lattice disorder in the Pd films before irradiation seems to be necessary for the achievement of superconductivity.

Figure 1 shows the occurrence and the further increase of the superconducting transition temperature, T_c, versus the dose of He atoms passing through two different Pd films. The 400-Å-thick film (curve *a*) was condensed *in situ* at 4.2 K and immediately irradiated, whereas the 200-

TABLE I. Evaporation conditions.

Evaporation source	W ribbon, BeO oven, electron gun
Substrate	SiO_2, Al_2O_{31}, Si
Substrate temperature	4.2–300 K
Pressure	2×10^{-10}–10^{-7} Torr
Evaporation rate	2–80 Å/sec
Thickness	50–1000 Å

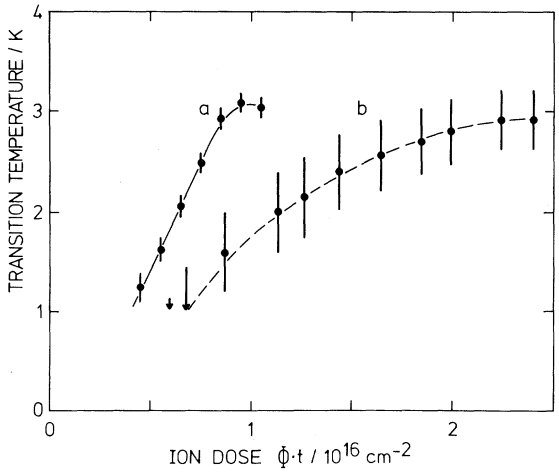

FIG. 1. Transition temperature of Pd films vs dose Φt of irradiating He^+ ions at 130 keV. (a) 400-Å Pd condensed at 4.2 K; (b) 200-Å Pd condensed at 200 K and annealed to 300 K.

Å-thick film (curve *b*) was condensed at 200 K and annealed to 300 K before cooling down to 4.2 K and irradiating it. In both cases superconductivity is achieved with about the same maximum transition temperature of 3.2 K after He^+ irradiation at low temperatures. From this behavior one can conclude that the maximum T_c does not depend on the special evaporation conditions. However, the width of the superconducting transition is much smaller in the quench-condensed case. Here the superconducting phase seems to be built up more homogeneously out of a disordered film. In this case also the maximum T_c value is achieved at a lower He dose compared to the sample annealed at room temperature. Obviously, the superconducting state can be formed more easily by irradiation if the starting material has already a high degree of lattice disorder. This conclusion is in qualitative agreement with the fact that after annealing to 500 K no superconductivity above 0.2 K could be obtained by low-temperature irradiation up to a He^+ dose of 5.3×10^{16} cm^{-2}.

The following experiment was performed to determine whether a special type of lattice disorder as produced by low-temperature irradiation is necessary for the occurrence of superconductivity. Different degrees and kinds of lattice disorder were produced as follows. A 400-Å-thick Pd film was quench condensed at 4.2 K. The high degree of lattice disorder in the resulting polycrystalline Pd was reduced by stepwise annealing to room temperature. The resulting resistivity ρ as a function of temperature is given in Fig. 2(a). Annealing of the quench-condensed Pd leads to an irreversible decrease of resistivity. At various annealing temperatures the Pd

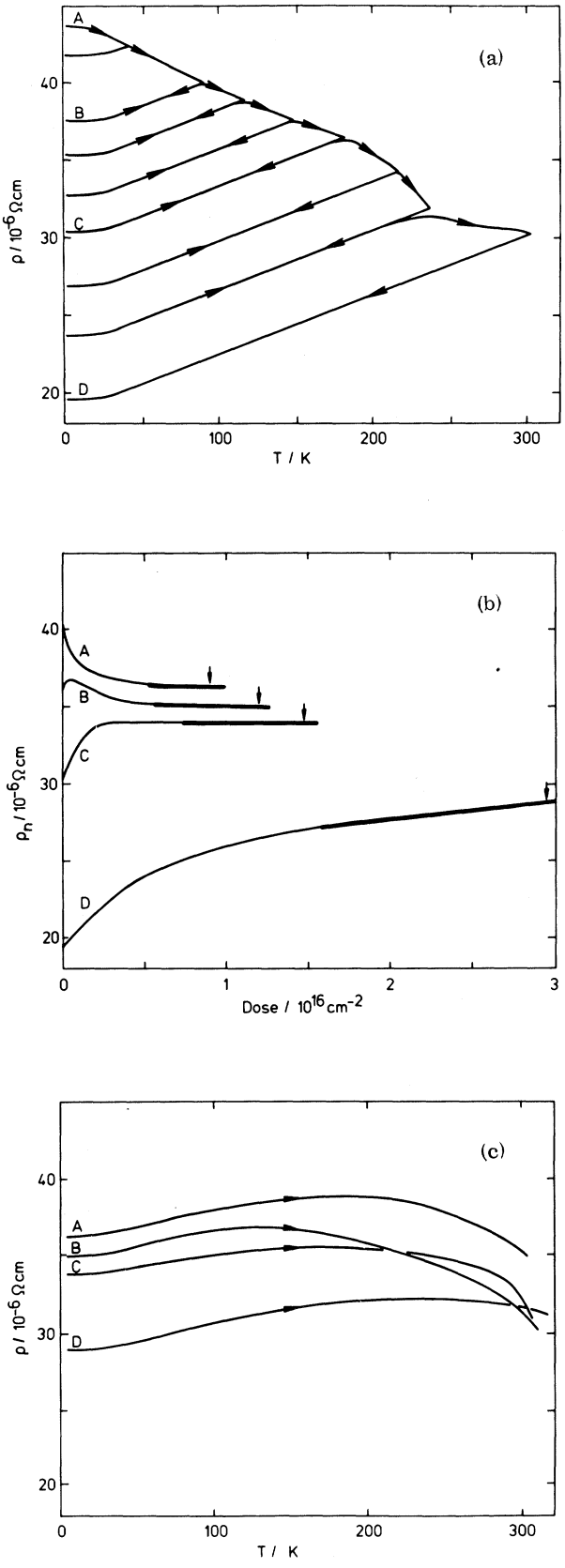

FIG. 2. Behavior of resistivity of 400-Å-thick Pd films condensed at 4.2 K. (a) Resistivity vs temperature. At different annealing temperatures the Pd was cooled down to 1.0 K and checked in vain for superconductivity. The capital letters represent different annealing stages: $A\cong 8$ K, $B\cong 90$ K, $C\cong 180$ K, and $D\cong 300$ K. (b) Residual resistivity of differently annealed Pd films [corresponding to *A*, *B*, *C*, and *D* of (a)] vs irradiating dose of He^+ ions with 130 keV, and at a flux $\Phi \lesssim 5\times 10^{11}$ cm^{-2} sec^{-1}. The thicker lines represent regions where superconductivity occurs, and T_c increases from 1.0 K (the detection limit in this experiment) to its maximum value of 3.0 K (indicated by the arrows). (c) Annealing curves of the Pd films described above after completion of the low-temperature irradiation.

is cooled down again to 1.0 K. This leads to a reversible decrease of resistivity with a constant slope above 40 K. Thus the annealing steps end up in a more reduced degree of lattice disorder. In all cases no superconductivity in this nonirradiated but disordered sample could be detected above 1 K. This result demonstrates that Pd cannot be made superconducting by quench condensation.

In further experiments, four 400-Å-thick Pd films were condensed in a similar way at 4.2 K. Three of them were annealed to stage *B*, *C*, and *D* of Fig. 2(a), cooled down to 4.2 K, and irradiated. Figure 2(b) shows the resulting change of resistivity ρ_n at 4.2 K with increasing He^+ dose. In the unannealed sample, ρ_n decreases as a result of radiation annealing. However, ρ_n of sample *D* (300-K annealing) increases with dose because of the addition of lattice defects. The behavior of ρ_n of sample *B* (90-K annealing) demonstrates that two different kinds of lattice defects are involved: one produced by irradiation and another produced by quench condensation. Irradiation produces new defects and anneals the old ones, resulting in a maximum of ρ_n versus dose in sample *B*. Superconductivity occurs in all four samples after irradiation as indicated by the thicker line in Fig. 2(b). In this region, superconductivity of the samples starts at 1.2 K, and increases with dose similar to Fig. 1. T_c reaches its maximum value at doses indicated by the arrows. These results clearly demonstrate again that superconductivity can be more easily achieved by irradiation if the starting Pd is highly disordered.

Figure 2(c) shows the annealing behavior of the irradiated samples *A*–*D*. The difference in the annealing behavior after quench condensation [Fig. 2(a)] and irradiation [Fig. 2(c)] illustrates the different kind of lattice defects involved in both processes.

In the following we will consider first what type of defects could be consistent with the observed dependence on dose and annealing history of the sample and second how irradiation-induced defects might produce superconductivity. In contrast to the evaporation, the irradiation at low temperatures can produce vacancies and Pd atoms located at interstitial sites (Frenkel pairs). The threshold energy for the production of Frenkel pairs could be reduced in a disordered material because of the loosely bound atoms at grain boundaries and other irregularities. If superconductivity is related to the formation of Frenkel pairs, this assumption could explain the fact that the superconducting phase can be more easily formed out of a highly disordered material.

The occurrence of interstitial atoms should widen the lattice. In fact we observed an increase of the lattice constant by 0.4% at 4.2 K in the irradiated superconducting state of Pd. This enormous effect—corresponding to about 2% interstitials—is a hint that not only Frenkel pairs are produced but perhaps also agglomerations of interstitials or vacancies. Such agglomerations could be achieved as a result of rather high local temperatures during the irradiation. These rather stable defects could explain the fact that the superconducting phase is rather insensitive to annealing but very sensitive to the ion flux.[10] The highest values of $T_c = 3.2$ K can be observed by irradiation with the lowest ion flux, $\Phi = 10^{11}$ cm^{-2} sec^{-1}.

How can these defects introduced by irradiation be responsible for the superconductivity in Pd? From band-structure calculations it is known that the Fermi level of crystalline Pd is located in a narrow peak (width < 0.1 eV) of the density of states.[11,12] It is reasonable to assume that the defects introduced by irradiation lead to a smearing of the Fermi surface, and thus to a reduction of $N(0)$. There is experimental evidence for this effect in Ar-sputtered Pd.[13] A reduction of $N(0)$ leads to a decrease of the Stoner enhancement factor. As a result, the strong spin fluctuations would be diminished and superconductivity might be possible. This assumption does not take into account a possible contribution from enhanced electron-phonon coupling due to weakened phonon modes in disordered Pd or optic phonon modes of interstitial Pd atoms.

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Electron-Spin Relaxation by Tunneling States in β-Al_2O_3:Na

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Spin relaxation measurements on a color center in the conduction plane of β-Al_2O_3:Na reveal an exceptionally fast rate with an anomalous temperature and microwave frequency dependence. The data are quantitatively described by a mechanism involving the coupling of a color center to the phonon-induced relaxation of a nearby localized two-level tunneling state. The required density of such states is nearly the same as that used to explain the low-temperature properties of β-Al_2O_3:Na.

In addition to being widely studied as a fast ionic conductor, sodium β-alumina is of interest because its low-temperature properties resemble those of a glass.[1-5] These properties of the β-aluminas, like other amorphous materials, have been explained in terms of the phenomenology of localized tunneling states (LTS).[6,7] We have observed an anomalous temperature and microwave frequency dependence in the electron spin relaxation rate of a paramagnetic center produced in the conduction plane of β-Al_2O_3:Na by low-temperature irradiation. These anomalies are satisfactorily explained by a density of tunneling states which also predicts the specific heat, thermal conductivity, and dielectric susceptibility data reported by Anthony and Anderson.[4]

The absorption derivative spectrum of the center is shown in Fig. 1. It has been independently observed and reported by O'Donnell, Barklie, and Henderson.[8] The intensity ratios in the eleven-line hyperfine pattern are characteristic of an electron interacting with two equivalent $I=\frac{5}{2}$ nuclei. From the anisotropy of the principal g factors and the magnitude of the hyperfine splitting, O'Donnell, Barklie, and Henderson argue convincingly that the defect is an F^+ center, i.e., an electron trapped at an oxygen vacancy, at the $O(5)$ site.[9] This site is 0.168 nm from the Al nuclei and 0.323 nm from Na ($I=\frac{3}{2}$) nuclei in the unperturbed lattice.

Our relaxation measurements were made at X and Ku band microwave frequencies using the pulse saturation and recovery technique. Spectrometer details have been published elsewhere.[10,11] None of the recoveries was strictly

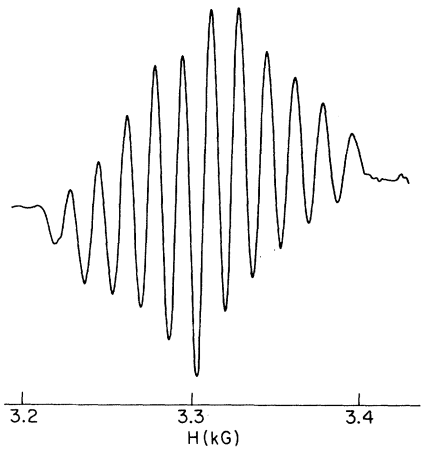

FIG. 1. Derivative of the EPR absorption spectrum from a color center in the conduction plane of β-Al_2O_3:Na as measured at 77 K and 9.3 Ghz, with $\vec{B}$ parallel to the c axis.