Magnetism of V, Mo, and Co surface impurities on Pb measured by their pair-breaking effect

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Thin films of Pb are covered *in situ* with submonolayers of V, Mo, and Co in the range between 0.01 and 1 monolayers. If the surface impurities are magnetic they will reduce the superconducting transition temperature of the Pb film. From the reduction of T_c the magnetic dephasing rate of the surface impurities $1/\tau_s$ and their magnetic cross section σ_s are calculated. We find that single V surface impurities are magnetic, while single Mo and Co impurities are nonmagnetic. Co surface clusters are magnetic. [S0163-1829(98)05305-3]

If one covers the surface of a nonmagnetic metal with a monolayer of a nonmagnetic transition metal one has a chance to observe magnetic moments in the transition-metal atoms. This has been predicted in a number of theoretical papers.[1–5] Most intensively studied are monolayers of $4d$ metals on the surface of noble metals. Unfortunately there is not yet an agreement with the experimental results on these systems.[6–8] More recently the numerical calculations have been extended to the magnetic properties of single transition-metal atoms on the surface of noble metals[9,10] showing an enhanced tendency towards a magnetic moment. Experimentally we observed fully magnetic V and Mo atoms on the surface of Au.[11,12] Both, V and Mo are nonmagnetic in their bulk state. In these investigations we used the method of weak localization as a tool to detect the magnetic character of the transition-metal atoms. In this paper we have two goals. One is to extend the investigation to systems where the substrate is polyvalent. A large number of polyvalent metals are superconducting. Our second goal is to show that the superconductivity itself, such as the superconducting transition temperature, can be used to detect the magnetic character of the transition-metal atoms on the surface of the superconductor. We use Pb as the substrate and superimpose it with three different transition-metal atoms, V, Mo, and Co.

Magnetic impurities in superconductors were intensively studied in the 1950's and 1960's (see, for example, the review by Maki[13]). They reduce the transition temperature due to their pair-breaking effect. If the impurities are homogeneously distributed in the superconductor then the reduction of the transition temperature is given by

$$\ln\left(\frac{T_{co}}{T_c}\right)=\Psi\left(\frac{1}{2}+\rho\right)-\Psi\left(\frac{1}{2}\right), \qquad (1)$$

where T_{co} is the transition temperature of the superconductor without the magnetic impurities, T_c is the reduced transition temperature due to the magnetism of the impurities, and Ψ is the digamma function. The parameter ρ is the pair-breaking parameter which is given by

$$\rho=\frac{\hbar}{2\pi k_B T\tau_s}=\frac{\hbar}{4\pi k_B T\tau_\phi}, \qquad (2)$$

with $1/\tau_s$ being the magnetic-scattering rate. The dephasing rate of the Cooper pairs is twice the magnetic-scattering rate $1/\tau_\phi=2/\tau_s$.

If we have a thin superconducting film with the magnetic impurities on one side of the film, then one can still use Eqs. (1) and (2) as long as the coherence length ξ of the superconductor at the temperature of the reduced T_c is large compared with the film thickness, i.e., $\xi>2d/\pi$. However, if one increases the concentration of the magnetic impurities on the (upper) surface of the film then the order parameter on this side of the film will be reduced and, in the limit of infinite pair breaking, the gap parameter $\Delta(z)$ or the Ginzburg-Landau wave function $\psi(z)$ (not to be confused with the digamma function Ψ) takes the form $\cos(z/\xi)$ with $d/\xi=\pi/2$ (z is the direction perpendicular to the film). Therefore one can determine the maximum reduction of T_c by magnetic impurities on one surface by the implicit condition

$$\xi(T_c)=\pi d/2.$$

The temperature dependence of the coherence length can be experimentally determined by the upper magnetic field perpendicular to the surface of the film B_{c2} according to the condition

$$2\pi\xi^2 B_{c2}=\Phi_0,$$

where $\Phi_0=h/2e$ is the superconducting flux quantum.

Our film samples are prepared by *in situ* condensation onto a quartz substrate at liquid-helium temperature. In a typical experiment a Pb film with a thickness of about 45 atomic layers and a resistance per square of about 100 Ω is condensed onto a quartz substrate. The vacuum is better than 10^{-11} torr. After the condensation the Pb film is annealed to about 40 K. The superconducting transition curve of the Pb film is measured. In addition we apply different magnetic fields up to 3 T perpendicular to the film. From the reduced transition temperature (we take the T_c at half the residual resistance), we obtain the coherence length of the Pb as a function of temperature.

In the following evaporation steps the V, Mo, or Co impurities are condensed on top of the Pb film. Generally we start with 1/100 of an atomic layer and increase the thickness by roughly a factor of 2 in each evaporation step. Each time the transition curve is measured in different perpendicular magnetic fields. In Fig. 1 the superconducting transition

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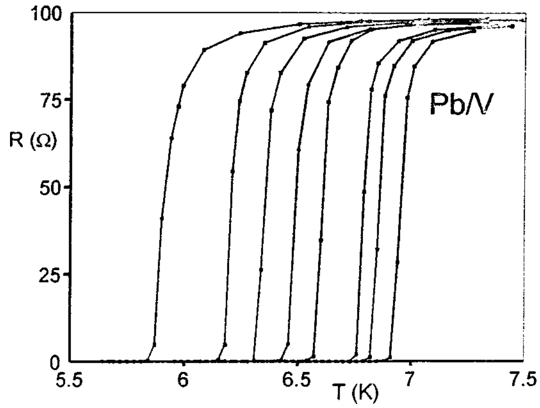

FIG. 1. The superconducting transition curves for a Pb film with increasing coverage of V. The V coverage is 0, 0.01, 0.02, 0.04, 0.1, 0.2, 0.4, and 1.0 atomic layers (from right to left).

curves are plotted for increasing V coverage. The Pb film has a thickness of 17.0 nm and a resistance per square of 97.6 Ω. The coverages are given in the figure caption. The transition temperature of the thin Pb film is 6.95 K compared with 7.2 K for pure bulk Pb. It has been known for a long time that thin superconducting films with a high resistance per square have a somewhat lower T_c than the bulk material (see, for example, Ref. 14).

In Fig. 2 the (reduced) transition temperature is plotted as a function of the coverage with the different d impurities. The coverage is measured in units of atomic layers. The inset in Fig. 2 shows the T_c dependence for small d impurity coverage. The three curves show quite a different behavior.

Vanadium: The T_c reduction due to V is linear for small V coverage with a relatively large slope. With increasing coverage the slope reduces considerably reducing the pair-breaking effect per V atom.

Molybdenum: The initial slope of T_c is rather flat and the total reduction is much smaller than for V.

Cobalt: For small Co coverage the T_c dependence looks close to the quadratic one (although the effect is too small to prove it quantitatively). With increasing Co coverages the slope increases strongly and reaches a constant value at roughly 0.1 atomic layers.

We restrict the following evaluation to the temperature range $T>6$ K. In this range the coherence length fulfills the condition $\xi > 2d/\pi$ [$\xi > \xi(6\ \mathrm{K}) = 15$ nm, $2d/\pi = 10.8$ nm]. In

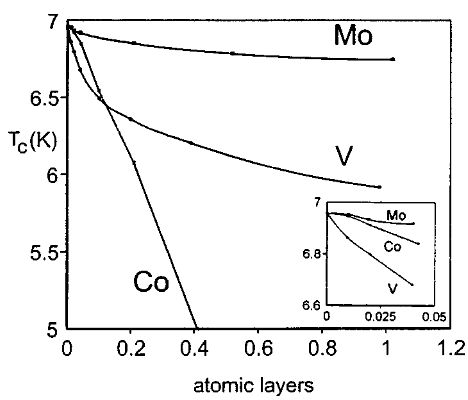

FIG. 2. The reduced transition temperature T_c as a function of the impurity coverage (in atomic layers) of V, Mo, and Co.

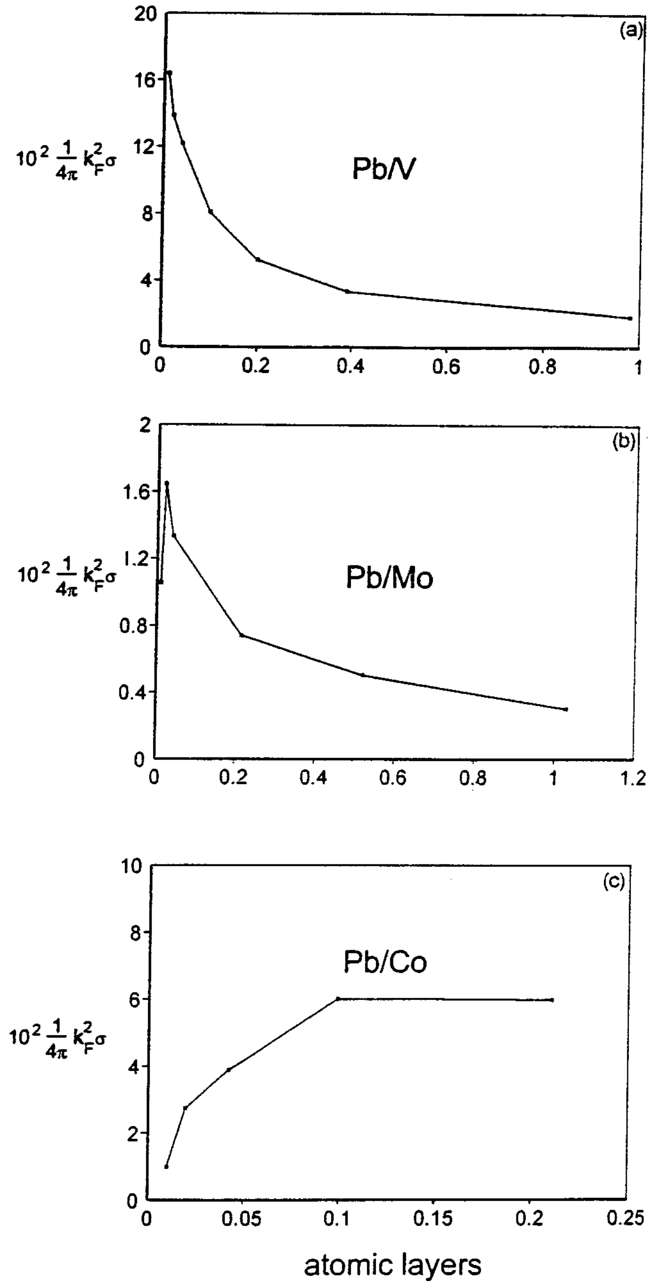

FIG. 3. The magnetic cross section (in units of $4\pi/k_F^2$) for (a) V, (b) Mo, and (c) Co on the surface of Pb as a function of the coverage.

this range Eqs. (1) and (2) can be used for the evaluation of the pair-breaking parameter ρ and the dephasing rate $1/\tau_\phi$. If we measure the thickness of the Pb film and the coverages of the impurities in units of monolayers then the (bulk) concentration c_d of the d impurities is given by

$$c_d = \frac{d_d}{\Omega_d^{2/3} d_{\mathrm{Pb}} \Omega_{\mathrm{Pb}}^{1/3}},$$

where d_d is the impurity coverage in atomic layers, d_{Pb} is the Pb thickness in atomic layers, Ω_d is the atomic volume of the magnetic impurity, and Ω_{Pd} is the atomic volume of the Pb host. Finally we obtain the magnetic-scattering cross section $\sigma_s = 1/(c_d v_F \tau_s)$. In Figs. 3(a)–3(c) we have plotted the magnetic cross section as a function of the transition-metal coverage. The magnetic cross section is given in units of $4\pi/k_F^2$ so that it is dimensionless. For single surface impurities of V the cross section is $\sigma_s k_F^2/4\pi = 0.17$. It decreases by an order of magnitude for a monolayer of V on Pb. The value for single V surface impurities on Pb is quite similar to the value of 0.15 which we observed for V surface impurities on Au.[11]

For Mo surface impurities the magnetic cross section is, by an order of magnitude, smaller than for V. Furthermore the magnetic cross section decreases for very small coverages (0.01 atomic layers). The dephasing is most likely maximal for pairs of Mo. Even the pairs do not have a full magnetic moment but only fluctuating moments. In single Mo surface impurities the (fluctuating) moment is still further suppressed.

For Co surface impurities the magnetic cross section is (within the accuracy of the measurement) linear at small coverages and therefore single Co surface impurities are nonmagnetic. However, the magnetic-scattering cross section increases with increasing coverage which indicates that clusters are magnetic. It reaches a constant value of about 0.06 for coverages above 0.1 atomic layers. We compare this result with the one for Co on Au.[15] Here single Co impurities were magnetic with the magnetic cross section of 0.085.

Our experiments prove that the reduction of T_c in small superconducting films can be used to investigate the magnetic character of surface impurities. Our group investigated in recent years the magnetic properties of $3d$, $4d$, and $5d$ impurities on the surface of noble-metal films. There we used the method of weak localization. This method has several advantages compared with the T_c reduction: (a) it is by a factor of 100 more sensitive and (b) it permits a measurement of the *pair-breaking* parameter as a function of the temperature (while the T_c reduction yields only the pair breaking at T_c). But weak localization is much less effective in superconductors because other effects such as the Azlamazov-Larkin fluctuations and the Maki-Thompson effect are superimposed. Therefore the two methods complement each other nicely. So far we have focused our investigations with weak localization on noble-metal surfaces. Polyvalent metal surfaces have a stronger tendency to suppress magnetism than the noble-metal surfaces. For example, a monolayer of Ni on Cu is ferromagnetic,[16,17] while it is nonmagnetic on metallic Bi (Ref. 18) or Mg. It would be more appropriate to compare our T_c method on Pb with weak-localization measurements on a polyvalent substrate. We performed preliminary weak-localization experiments on Mg films with the surface impurities of V and Co. We found that single V impurities on Mg are magnetic, while single Co impurities are not. This agrees nicely with our present results on Pb.

There is another reason why a comparison between the methods of T_c reduction and weak localization is interesting. The diagrams for the dephasing, i.e., the pair breaking, are identical. However, weak localization is a single-particle property, while superconducting pair breaking involves two (time-reversed) electrons. During the 1960's one observed so-called *pair weakening* in superconductors with $4d$ and $5d$ impurities. One suggested cause was that the Coulomb repulsion between the two electrons of a Cooper pair at the site of the impurity was responsible for the weak T_c reduction. Our weak-localization experiments observed fluctuating moments for d surface impurities (on Au). If those are also present in bulk superconductors they might provide an alternative explanation for the pair weakening. Therefore a comparison between the two methods might add to our understanding concerning the role of d impurities in superconductivity.

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