Brief Reports

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Exchange interactions of quench-condensed vanadium atoms on metal surfaces

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In situ studies of quench-condensed V atoms on Pb, Al, Au, and Ag substrates show that V atoms form isolated magnetic moments for an average thickness $d \lesssim 0.03$ monolayer (ML). For $d \gtrsim 0.03$ ML antiferromagnetic coupling between V atoms is detected and increases. At $d \simeq 1.5$ ML the interaction becomes predominantly ferromagnetic. On Au and Ag surfaces the moment is comparable to that of an isolated Fe atom, whereas on Pb or Al the moment is less by a factor of about 7.

Vanadium in bulk has no static magnetic moment and no long-range magnetic order. However, recently magnetic behavior has been predicted theoretically[1–6] and observed experimentally[7–10] for thin films and surfaces of V. Measurements of the susceptibility of very small V particles made by Akoh and Tasaki[7] and analyzed by Grempel and Ying[6] implied the existence of an antiferromagnetic (AF) surface layer. Ohnishi *et al.*[2,3] predict a paramagnetic state for the V(100) surface. On the other hand, Rau *et al.*,[8] using electron-capture spectroscopy, found that the V(100) surface was ferromagnetic (FM) with a Curie temperature $\simeq 540$ K. Theoretical groups[1,4] have predicted a magnetic moment (μ) of $1.75\mu_B - 3\mu_B$ per V atom for a monolayer of V on Au or Ag (001) surfaces. Fu *et al.*[1] and Gay and Richter[4] predict FM ordering for such layers, whereas Blügel *et al.*[5] predict AF ordering. Recent experiments by Rau *et al.*,[9] using an epitaxial V film 1–7 monolayers thick over a Ag(100) surface, measured a FM interaction of the topmost layer for all thicknesses of V. Inverse photoemission results by Drube and Himpsel[10] suggest a large ferromagnetic exchange splitting for V on Ag(111). On the other hand, Stampanoni *et al.*[11] using spin-polarized photoemission found no evidence of ferromagnetism in a V monolayer on Ag(001). In our present experiments, we follow *in situ* the magnetic behavior of quench-condensed V from well-isolated atoms to monolayer average coverage and beyond on Au, Ag, Al, and Pb substrates. We clearly find AF interactions between V atoms starting at about 0.03 monolayers (ML), changing over to ferromagnetic interactions by $\simeq 1.5$ ML thickness of V, with a strong dependence of μ on the substrate material. This *in situ* observation of the onset of AF interactions among V atoms and the changeover to ferromagnetic interaction for thicker layers has not been seen in any other system that we know of.

The effect of isolated magnetic impurities on the superconducting transition temperature was analyzed by Abrikosov and Gor'kov[12] (AG) using the Born approximation for exchange scattering. Skalski *et al.*,[13] using the AG theory, calculated the impurity concentration dependence of the order parameter. The effects of interactions between magnetic moments on the behavior predicted by AG theory have been reviewed by Fulde and Keller[14] and Vonsovsky *et al.*[15] A general result is that FM interactions cause more rapid decrease of the superconducting order parameter Δ than the AG theory for noninteracting impurities, whereas AF interactions cause less rapid decrease of Δ than the AG theory. Roshen and Ruvalds[16] have recently calculated such effects for large impurity concentrations coupled by a Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and find strong deviations of Δ from the AG theory.

The experiments presented in this Brief Report use a rf surface-impedance method which has been described in detail elsewhere.[17,18] On a sapphire substrate a NbN thin-film meander line is the inductance of a 14-MHz LC circuit driven by a tunnel diode. A thin film of superconducting Pb is deposited on the liquid-helium-cooled substrate with the Pb film being separated from the meander line by a 1-μm-thick insulator. Shielding currents in 90-Å-thick Pb film decrease the effective inductance of the LC circuit and raise its resonant frequency f by about 100 kHz. Magnetic material then deposited on the Pb film decreases the number of superconducting pairs in the Pb, which in turn decreases f. During the deposition, the oscillator frequency is recorded as a function of the average deposited film thickness d as measured by a quartz crystal thickness gauge.

Figure 1 shows measurements of V deposited on Pb.

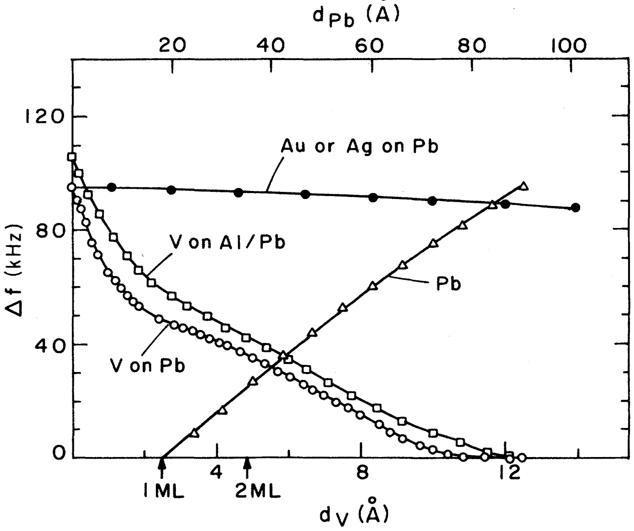

FIG. 1. Changes in the oscillator frequency as a function of film thickness as measured during the deposition of various metals over the inductor. Note the difference in thickness scale for Pb and other metals. Thickness scale for Ag or Au is the same as that of V.

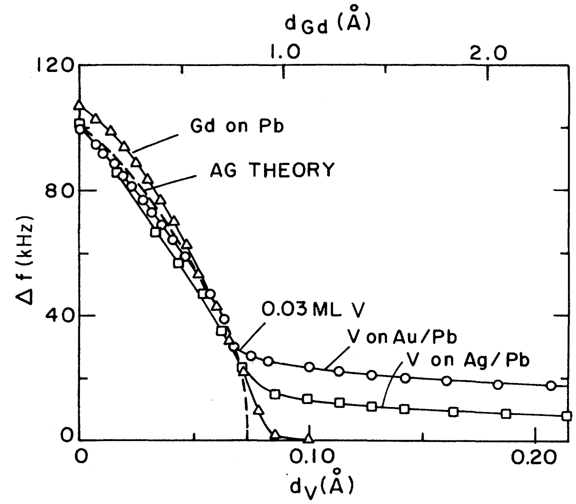

FIG. 2. Frequency changes of the oscillator when V is deposited over Au/Pb and Ag/Pb films. Also shown is the behavior of Gd metal deposited on Pb for comparison. The dashed line is proportional to the expected decrease in the order parameter due to magnetic impurities according to AG theory.

The substrate was first covered with 100 Å of SiO, which caused no significant frequency change. Pb was then deposited and at a thickness $d \gtrsim 18$ Å the superconducting Pb film acted diamagnetically to decrease the effective inductance of the meander line and increase the oscillator frequency almost linearly with d. At $d = 90$ Å (upper scale) the change in frequency $\Delta f \simeq 95$ kHz and the Pb deposition was stopped. Next, V deposited on the Pb caused the decrease in f versus d (lower scale). The decrease in f, reflecting a decrease in the superconducting order parameter, is to be expected with materials which form local magnetic moments. The exact interpretation of the shape of the curve will be discussed below. In a separate experiment, Al 14 Å thick was deposited over the Pb before the V was deposited. It is seen that the dependence of f on d in the two cases was very similar.[19] Also shown in Fig. 1 is the dependence of f on d for Ag or Au over Pb, showing that there is only a very slight decrease in the superconducting carrier density in the Pb because of a proximity effect with a normal metal.

Figure 2 shows the decrease in f when V is deposited on 14 Å of Au (or Ag) deposited over the 90-Å Pb film. The initial decrease in f is about seven times more rapid than that shown in Fig. 1 for a 90-Å Pb film without the Au or Ag (note the difference in the scale of d in Figs. 1 and 2). This result implies a much greater magnetic moment for V on a Au or Ag substrate than on a Pb or Al substrate. The dashed curve shows the AG theory[13] for noninteracting impurities and agrees with experiments on bulk alloys with dilute magnetic impurities. This curve is based on the assumption that the order parameter Δ of the Pb film is proportional to the frequency change Δf. This relationship is to be expected when the Pb thickness is less than the coherence distance since Δ measures the number of superconducting pairs and the proportionality between Δf and Δ previously was shown to be reasonably accurate.[18] The data for Gd on Pb agree with the AG theory, as would be expected, except for a small deviation close to d_c (the thickness of impurity at which Pb became normal at 4.2 K and f returned to its initial value before the Pb was deposited). The slight deviation from the AG curve near d_c may result from the random nature of the deposition. Although V on Au/Pb or Ag/Pb follows the AG curve for low coverage, at $d = 0.07$ Å or 0.03 ML the curve deviates sharply from the AG theory and the frequency decreases only very slowly with increased average thickness. This behavior is similar to that observed for Cr and Mn deposited on Pb at somewhat thinner coverage. For Cr and Mn this deviation from the AG theory was attributed to the AF interactions between Cr and Mn atoms.[18] Such AF interactions have been shown theoretically[14–16] and experimentally[20,21] to decrease the depairing effect of magnetic impurities, similar to that seen in the present case.

Figure 3 combines measurements of Δf versus d for low coverage for various materials. For each material the average thickness scale is adjusted to give the same initial slope. All of the materials can be fitted to the AG curve at low enough coverage. The sharp deviation from the AG theory for V on Au or on Ag begins at a coverage of about 0.03 ML. This is to be compared with the sudden deviation of Cr and Mn from the AG theory at a coverage of about 0.006 to 0.012 ML, respectively. For V on Pb (without the Au or Ag) the deviation from the AG theory becomes noticeable at 0.06 ML. All of these deviations are indications of interactions which decrease the depairing effect on the superconductor and we interpret these interactions as being AF, as in the case of Cr and Mn. The onset of the AF interactions is at smaller coverage as the magnitude of the magnetic moment increases.

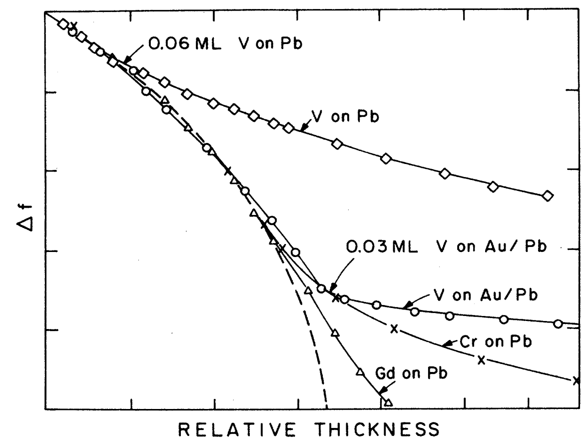

FIG. 3. Comparison of various systems by adjusting the thickness scales to give the same initial slope for all. The data on Cr over Pb are from our earlier work (Ref. 19). AG theory (dashed line) is also shown.

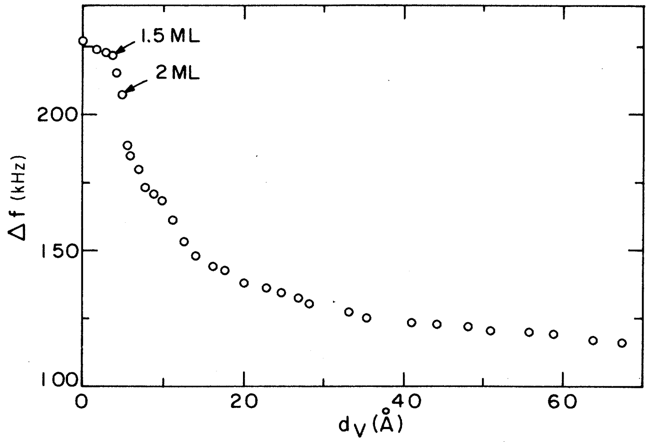

FIG. 4. Frequency change when V is deposited over a 14 Å Au film which is covering a thicker (180-Å) Pb layer showing the behavior of V on Au at larger coverages.

Consider now the detailed shape of the V on Pb curve in Fig. 1. For values of $d > 0.14$ Å the Δf versus d curve has a positive curvature up to $d \simeq 1.25$ ML, but from 1.25 to 3.0 ML the curvature is negative. Such a negative curvature in the Δf versus d curve was seen for Ni and Fe at thicknesses where ferromagnetic ordering took place,[17] and also as given theoretically[14–16] and seen experimentally.[20,21] We interpret the data of Fig. 1 as follows. For $d \gtrsim 0.06$ ML the RKKY coupling through the conduction electrons of the Pb leads to AF interactions. At much greater coverage near 1.25 ML the interaction becomes predominantly FM. In our earlier work[18] on V on Pb, we have seen similar behavior (although not well understood at that time) where the complete picture of V interactions was not evident since the thickness range covered was insufficient.

Figure 4 shows the effect of depositing a comparatively thick layer of V on 14 Å of Au covering 180 Å of Pb. The thicker Pb film was necessary to prevent it from being driven normal with a thicker film of V. The initial slow drop in frequency corresponding to a continuation of Fig. 2 is followed by a very steep drop in frequency starting at 1.5 ML. This drop is at the same value of d that the more subtle effects were seen at for V on Pb and Al/Pb, shown in Fig. 1. The result for Au/Pb strongly reinforces the conclusion that this more rapid depairing indicates a ferromagnetic interaction at close to 1 ML. The more gradual decrease in f at larger values of d presumably reflects the decreased effect of added layers of V on the Pb film as this Pb film is more than one coherence length thick.

It is reasonable that, as the coverage gets greater and the separation of isolated magnetic moments decreases, indirect RKKY interactions through the conduction electrons should change sign from AF to FM because of the oscillatory nature of the RKKY interactions. However, when we consider that the average coverage at which this becomes detectable corresponds to an average separation of V atoms by about 5.5 atomic diameters, it at first appears that this coverage is too small since the characteristic distance of the RKKY interaction is $(2k_F)^{-1}$. To investigate this question we made a simple statistical calculation. Atoms were distributed randomly in 484 close-packed sites in two dimensions and the number of isolated atoms N_i, nearest neighbors N_{NN}, and next-nearest neighbors N_{NNN} were determined as a function of average thickness d. For small d the atoms were isolated. For $d = 0.03$ ML, $N_{NNN} \simeq N_i/3$; for $d = 0.065$ ML, $N_{NNN} \simeq N_i$; and for $d = 0.080$ ML, $N_{NN} \simeq N_i \simeq N_{NNN}/2$. A random deposition of atoms into sites without clustering for fairly high melting point materials deposited on a 4.2-K substrate is consistent with estimates of surface diffusion at this temperature.[22] Any clustering would lower the value of d at which interactions become significant in their effect on depairing of the superconductor. Although this is a crude model of the experimental conditions, it shows that the observed onset of interactions is at reasonable coverages. Unfortunately, there is no surface technique which has been able to determine the position of individual atoms deposited on a disordered surface at low temperature,[23] so that this model can be checked at present. However, we plan to adapt a low-temperature scanning tunneling microscope for future studies of these effects.

The exchange constant, J, for the impurity atom and the conduction electron can be estimated[18] from these measurements using the theory by Skalski *et al.*[13] for isolated magnetic impurities. The reductions of the transition temperature (ΔT_c) per at. % of V on Au (or Ag) and Pb (or Al) are, respectively, 20 and 3.5 K, whereas the exchange constants are 66 and 5 meV, respectively. These values may be compared with the corresponding values of 36 K and 18 meV for Fe on Pb, and 59 K and 37 meV for Cr on Pb, obtained from our earlier work.[18]

The present measurements clearly show that isolated V atoms on the surface of Pb, Al, Ag, and Au (and presumably other metals) have a magnetic moment. On Ag and Au the magnitude of this moment is about equal to that of Fe. On Pb or Al the magnitude of the moment is about seven times less. There is strong evidence that interactions between randomly spaced V atoms at fairly low coverage are antiferromagnetic and that at a thickness of about one atomic layer the interactions are predominantly ferromagnetic. The results agree with theoretical predictions of a high magnetic moment for a monolayer of V on Ag or Au (Refs. 1 and 4) and they agree with some experimental results,[9,10] but apparently disagree with a spin-polarized photoemission result.[11] This disagreement might be explained by a calculation of Gay and Richter[4] that predicts that the magnetization of a monolayer of V on Ag is perpendicular to the plane of the monolayer and thus would not have been observed. The present measurements on quench-condensed material are not necessarily to be compared with epitaxial material or idealized theoretical calculations. However, the present results imply that the interactions are localized enough so that lattice disorder is not a dominant factor. The effect of the host lattice on the magnetic moment of V is quite similar to that found in the case of Ni, which in itself is quite interesting. In the case of Ni, the suppression of its magnetic moment when in contact with *sp* metals like Al and Pb has been attributed to *sp-d* hybridization, whereas such coupling is not significant with noble metal substrates.[24] Also, magnetic interactions in quench-condensed Ni films showed the same dependence on the substrate material as that found for epitaxially grown Ni on various substrates.[24]

The principal result of this work on V is to show explicitly the change in sign of the exchange interaction at a surface as a function of separation.

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