tex core in a superconductor, which does increase.

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Field-Ion Microscope Observations of Indirect Interaction between Adatoms on Metal Surfaces*

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From field-ion microscope kinetic and equilibrium experiments with rhenium adatoms on W(110) planes it is found that the interaction potential energy between two adatoms exhibits an oscillatory behavior. The cohesive energy between two adatoms is very small, only ~0.16 eV at the closest separation. These observations are in general agreement with the indirect adatom interaction models as proposed and discussed by various investigators.

When an atom is adsorbed on a metal surface, the electron gas is perturbed. This perturbation is long ranged, and the adsorption of one atom will influence the adsorption of another atom over large distances where direct interaction of the two adatoms is negligible. The indirect atomic interaction was first realized by Koutecky[1] and subsequently investigated by Grimley,[2] Newns,[3] and Einstein and Schrieffer.[4] The interatomic potential resulting from the indirect adatom interaction exhibits oscillatory behavior reminiscent of Ruderman-Kittel-Kasuya-Yosida interactions[5] and Friedel oscillations[6] in solids. Both Grimley[2] and Einstein and Schrieffer[4] find that the indirect interaction is strong when the virtual adatomic level is near the Fermi level, and is weak when the virtual level is far below the Fermi level. The oscillatory period depends also on the energy of the virtual adatomic level. The latter authors further find that the interaction at nearest-neighbor distance is about an order of magnitude smaller than the adsorption energy of an adatom with the substrate lattice. They also succeeded in explaining the superlattice structures of chemisorbed atoms on solid surfaces as found by the low-energy electron-diffraction technique using the indirect adatom interaction. The indirect interaction is thus fundamental to the understanding of solid surfaces. It is desirable to have independent direct experimental evidence to confirm the theoretical predictions as well as to substantiate the novel interpretation of the superlattice structures. However, it is important to realize that whatever experiments one performs, a quantitative agreement with the theories cannot be expected and is not very meaningful because of the experimental difficulties involved in realizing the idealized theoretical models. One should instead focus attention on observing the general features as predicted by the models.

Experimental evidence of the Friedel oscilla-

tion and the oscillatory interatomic potential in solids[7] has been obtained with NMR,[8-10] x-ray,[11] and neutron-diffraction techniques.[12] It has not yet been demonstrated that such techniques are also applicable to the investigation of surface processes. The field-ion microscope[13] (FIM), with its unique atomic resolution, seems to be the most appropriate instrument for investigating the indirect adatom interaction. We report here experimental evidence of such an interaction using field-ion microscopy. The FIM and the general operational procedures used in this experiment have already been described in detail elsewhere.[14]

It has been found earlier by Bassett and Parsley[15] that metallic adatoms on a metal plane combine rapidly into closely bound clusters once the substrate temperature is high enough for the adatoms to have sufficient mobility. We on the other hand found that the rhenium adatoms on the W(110) plane repelled each other at low temperatures.[14] In one experiment, we deposited seven Re adatoms on an approximately circular W(110) plane ~60 Å in diameter and then heated the substrate to ~330°K for several tens of heating periods of 180 sec each. The imaging field was turned off during the heating. No closely bound cluster was ever observed. Closely bound Re clusters, however, are occasionally formed when the substrate surface is heated above 400°K. Figure 1(a), micrograph (i), shows an example of the most closely bound Re_2 clusters on a W(110) plane. The bond length is believed to be 2.74 Å, the nearest-neighbor distance of the substrate lattice.[14] At low temperatures loosely bound Re_2 clusters are often observed. Two Re atoms seem to migrate together maintaining a separation of 6–7.5 Å. It suffices to conclude from these observations that the interatomic potential between two Re atoms on the W(110) plane exhibits at least two relative minima at ~2.74 and ~6.8 Å, respectively, and a relative maximum somewhere between the two minima. Above 400°K, the probability for overcoming the relative maximum becomes appreciable, and the closely bound Re_2 clusters are thus occasionally formed.

Quantitative information on the interatomic potential may be obtained by kinetic and equilibrium experiments.[16,17] In the kinetic experiment[15,17] one measures the dissociation time t of a cluster at a certain temperature T. The cohesive energy E_c is then obtained from

$$t \approx (h/kT)\exp[(E_d+E_c)/kT], \quad (1)$$

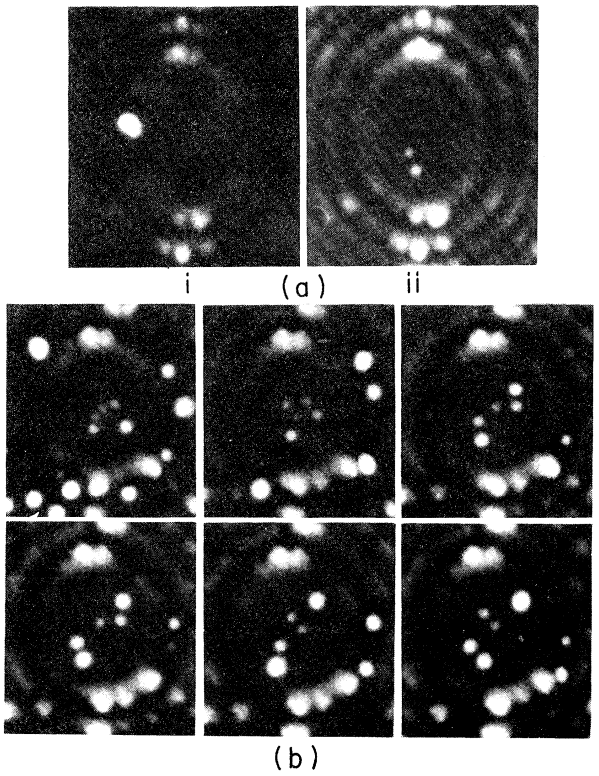

FIG. 1. (a) Micrograph (i), closest-packed Re_2 cluster formed above 400 K on a W(110) plane. (ii) Re_2 cluster now dissociated into a very loosely packed cluster. (b) Five Re atoms thermally deposited on a W(110) plane as shown in the upper left-hand micrograph. The rest of the micrographs are random selections of the same five Re atoms after various heating periods. A total of 34 heating periods were performed with the five atoms.

where E_d is the activation energy of surface diffusion, h is Planck's constant, and k is Boltzmann's constant. The kinetic experiment is suitable where the potential energy is sufficiently steep to allow no other bond length in the vicinity of the relative minimum one wishes to investigate. This is the case for the closest bound Re_2. At 390°K, Re_2 is found to dissociate in ~180 sec [Fig. 1(a), (ii)]. From Eq. (1), E_c is found to be ~0.16 eV when E_d is taken to be 1.01 eV.[17]

At larger separations, no rigid bond length is observed, and the equilibrium experiment can be performed. This is for comparison of the experimentally observed pair distribution function with that derived theoretically for noninteracting particles. An experiment with five Re atoms on a W(110) plane of radius ~30 Å is shown in Fig. 1(b). A total of 34 heating periods were performed at 320°K. Between two heating periods,

the atomic positions were recorded by photography. The atomic separations were then carefully mapped. The histogram shown in Fig. 2(a) is the pair distribution function obtained.

The pair distribution function $p(R)$ for N noninteracting particles randomly distributed over a circular plane of radius R, with $p(lR)d(lR)$ representing the number of atomic separations between lR and $lR+d(lR)$, can be shown to be given by

$$p(lR) = R^{-1}N(N-1)F(l), \tag{2}$$

$$F(l) = l(1-l)^2 + (2l/\pi)\int_{1-l}^{1} \cos^{-1}[(x^2+l^2-1)/2xl]x\,dx \text{ for } 0 \leq l \leq 1,$$
$$= (2l/\pi)\int_{l-1}^{1} \cos^{-1}[(x^2+l^2-1)/2xl]x\,dx \text{ for } 1 < l \leq 2. \tag{3}$$

Here l is a variable ranging from 0 to 2, and $F(l)$ represents the relative probability density for finding various atomic separations. It should be noted that $F(l)$ is independent of N. It can also be shown that

$$\int_{l=0}^{2} p(lR)\,d(lR) = \tfrac{1}{2}N(N-1), \tag{4}$$

which is the total number of atomic separations for N particles. The theoretical pair distribution function for noninteracting particles appropriate for the experimental conditions is shown in Fig. 2(b). By dividing the experimental pair distribution function with that theoretically derived for noninteracting particles, one obtains the pair correlation function $g(r)$, which is related to the potential of mean force $W(r)$ through[18]

$$W(r) = kT \ln[g(r)]. \tag{5}$$

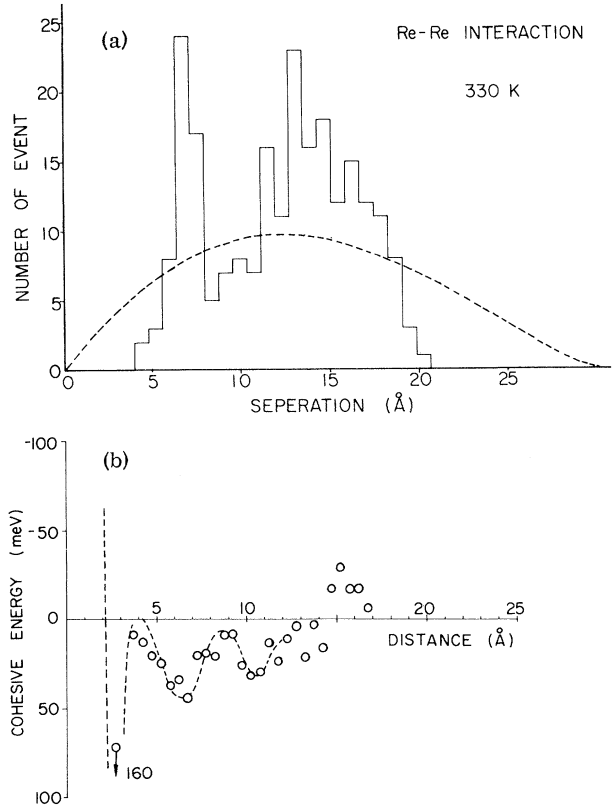

FIG. 2. (a) Histogram, pair distribution function obtained with five Re atoms. Dashed curve, theoretical curve for noninteracting particles. (b) Point at 2.74 Å obtained from the kinetic experiment described in the text. The rest of the data were obtained from the histogram shown in (a).

Figure 2(b) shows the potential of mean force derived from Fig. 2(a). The potential of mean force is related to the pair potential $u(r)$ through the Kirkwood or the Born-Green-Yvon integral equation.[19] $u(r)$ can in principle be derived from the experimental $g(r)$ by solving the integral equations self-consistently using numerical methods. The accuracy of the experimental data shown, as limited by the number of events obtainable with this particular experimental technique and the intrinsic nonuniform magnification of the FIM, does not allow us a meaningful derivation of $u(r)$ from the integral equations. It is, however, well known that in the low atomic density limit, $W(r)$ approximates $u(r)$ quite well. The number density ρ in this experiment, after being converted to three dimensions, corresponding to $\rho\sigma^3 = 0.012$ with σ representing the atomic diameter, is so small that $W(r)$ probably does not differ from $u(r)$ by more than a few percent at worst.[20] A second set of experimental data, again with five Re atoms on a W(110) plane ~30 Å diameter, is shown in Fig. 3(a). The pair potential, or more correctly the potential of the mean force, derived is given in Fig. 3(b). Within the experimental accuracy the two sets of data exhibit the same oscillatory structure. The statistical fluctuation and the nonuniform magnification of the FIM images tend to dampen the oscillatory amplitude, to shift the data points downward, and to wash out the structure at large distances. Within these difficulties, which are intrinsic to the technique, the described experiment provides the first straightforward evidence of the indirect ad-

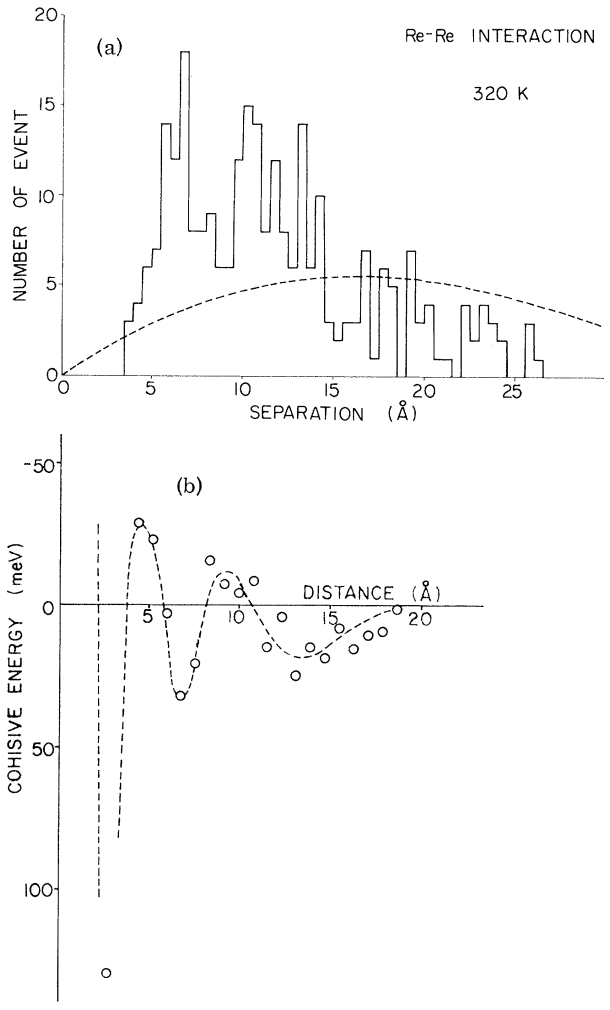

FIG. 3. (a) Another set of experimental pair distribution functions. (b) Cohesive energy derived from (a).

atom interaction. The magnitude observed is consistent with that predicted by Einstein and Schrieffer.[4] It is also comparable to the atomic interaction in aluminum.[7]

For W adatoms on the W(110) plane, the cohesive energy at nearest-neighbor distance is found to be ~0.26 eV. No long-range oscillatory structure was observed. The odd number of $5d^5$ electrons in Re atoms may be responsible for the enhanced oscillation observed. We do not know to what extent the observed potential is contributed from a direct adatom interaction. In any case, no long-range oscillatory structure is expected from direct atomic interaction.

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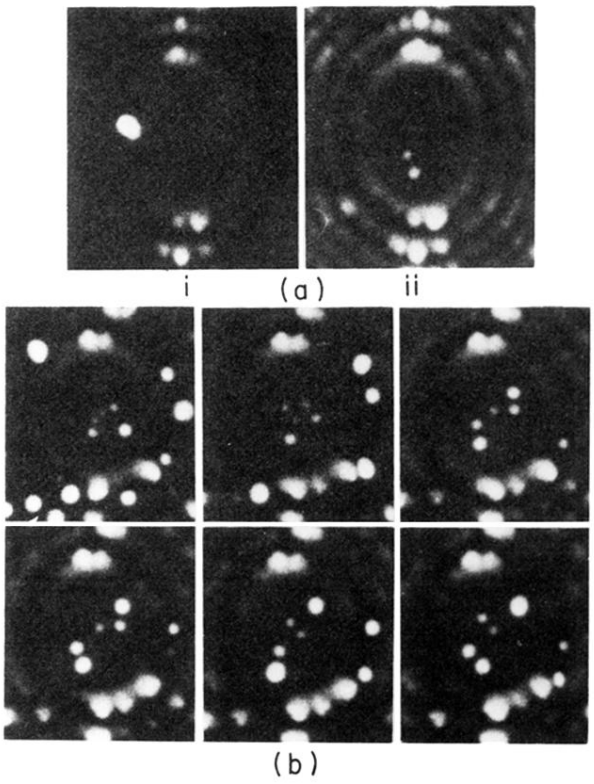

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