obviously reproduced by both calculations. The slightly deeper well depth of Wolniewicz (2.04 eV vs 1.85 eV for the Michels calculation) gives an extremely good fit to the data. The sensitivity of the JWKB calculations to slight changes in the well depth is clearly evident in Fig. 1 when one compares the cross sections determined from $V_M(r)$ and $V_W(r)$. Although the well depths differ by only approximately 10%, the JWKB calculation based on $V_M(r)$ is clearly out of phase with the experimental data in the vicinity of 20°.

It is believed that the agreement between the present experimental results and the calculations based upon the ab initio potential of Wolniewicz is a strong confirmation of the validity of his adiabatic calculations and also confirms that such calculations are capable of describing the dynamical problem of scattering at low collision energies.

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FIELD ADSORPTION OF INERT-GAS ATOMS ON FIELD ION EMITTER SURFACES*

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Theories of field ionization assume an atomically clean surface. Atom-probe experiments surprisingly revealed that the inert imaging gases are adsorbed at the field ion emitter. It is shown that this adsorption is due to a short-range field-induced dipole-dipole interaction. Adsorption at the apex of the protruding surface atom has considerable consequences for the mechanism of field ionization and field evaporation.

It is generally assumed that field ion emitter surfaces, prepared by low-temperature field evaporation and subsequently kept at a field of 4 to 6 V/Å, are free of adsorbates despite the presence of approximately 1 mTorr of imaging inert gas and a small amount of residual gases.[1-3] The van der Waals binding of helium or neon on metals is too small to allow noticeable adsorption at liquid nitrogen or liquid hydrogen temperatures. The induced dipole attraction due to the inhomogeneous field around the tip is a long-range force causing a hopping motion of the gas atoms above the emitter surface rather than adsorption on it. Contaminating residual gases of lower ionization potentials cannot reach the surface as they are repelled following their ionization on the approach. The field ion microscope (FIM) images were therefore considered to represent clean surfaces. All the theoretical treatments[1-7] of the field ionization process except a qualitative consideration of field ionization above adsorbed foreign atoms[8] also assume the metal surfaces to be clean.

Nishikawa and Müller[9] had observed earlier that the quality of a helium ion image is improved by a small addition of neon. This has been explained by the enhanced thermal accommodation of the hopping helium atoms when they collide with temporarily adsorbed neon atoms rather that with the much heavier metal atoms. In atom-probe experiments Müller[10] found that He^+ and Ne^+ ions are coming off the surface with the application of the short desorption pulses used for the operation of this instrument. Further work[11,12] definitely established the field-induced adsorption of He, Ne, and Ar up to temperatures above 80°K. Field desorption of these gases is only possible at a field that also evaporates the surface metal atom. Compared with field evaporation in vacuum, this field is reduced by the image gas. Moreover, helium, and more rarely the other noble gases, may form molecular ions with the evaporating metal.

In this short note we shall demonstrate the following: (1) Adsorption of inert gas atoms on field ion-emitter surfaces is possible by a short-range field-induced dipole-dipole interaction. (2) The binding energy is largest when an inert gas atom sits at the apex of a surface metal atom. (3) The occurrence of field adsorption requires modifications of the theory of field ionization.

Before discussing field adsorption, we must consider the polarizability of metal surface

atoms. When an electric field F_0 is applied, the binding energy of the surface atom increases by an amount $\frac{1}{2}\alpha_M F_0^2$, where α_M is smaller than the polarizability of the free atom as the surface atom is partially immersed in the Fermi sea.[13] The surface polarizability α_M of kink-site atoms is obtained by measuring the rate of field evaporation,[14] and amounts to 3.44 Å^3 at the edge of a (110) lattice step. With such a large polarizability, the electric field in the immediate vicinity of the kink-site atom is drastically modified. An approaching imaging gas atom encounters the sum of the applied field F_0 and a dipole field due to the surface atom.[15] Therefore

$$\vec{F}_A = \vec{F}_0 + [3\hat{n}(\vec{p}_M \cdot \hat{n}) - \vec{p}_M]/d^3, \quad (1)$$

where d is the distance between the two atoms, $\hat{n}$ is a unit vector from the metal atom to the gas atom, and $\vec{p}_M = \alpha_M \vec{F}_M$ is the field-induced dipole moment of the metal atom. The same argument gives

$$\vec{F}_M = \vec{F}_0 + [3\hat{n}(\vec{p}_A \cdot \hat{n}) - \vec{p}_A]/d^3, \quad (2)$$

where $\vec{p}_A = \alpha_A \vec{F}_A$ is the field-induced dipole moment of the imaging gas atom. Using Eqs. (1) and (2), the potential energy of an imaging gas atom directly above a metal atom can be shown to be

$$U_A = -\tfrac{1}{2}\alpha_A f_A F_0^2, \quad (3)$$

where

$$f_A = \frac{(1+2\alpha_M/d^3)^2}{(1-4\alpha_M\alpha_A/d^6)^2} \quad (4)$$

is an enhancement factor due to field-induced dipole-dipole interaction. It is noted that f_A is a short-range factor with an effective range of the order of $2\alpha_M^{1/3}$ when $\alpha_A \ll \alpha_M$. Additionally, f_A depends on the chemical nature and the specific site of the surface metal atom through its polarizability α_M. The potential energies for a He atom at an applied field of 4.5 V/Å, for a Ne atom at 3.75 V/Å, and for a Ar atom at 2.2 V/Å when they are directly above a kink-site atom at a tungsten (110) plane are shown in the solid lines of Fig. 1. The polarizabilities used are $\alpha_M = 3.44$, $\alpha_{He} = 0.2$, $\alpha_{Ne} = 0.39$, and $\alpha_{Ar} = 1.6$ Å^3. The short-range field-binding energy (the potential energy at closest distance $r_M + r_A$, the sum of the radii of the two atoms) is given by

$$H_f = \tfrac{1}{2}\alpha_A(f_A - 1)F_0^2. \quad (5)$$

Using the atomic radii $r_W = 1.36$, $r_{He} = 1.22$, $r_{Ne} = 1.60$, and $r_{Ar} = 1.92$ Å, at the respective fields given above, the adsorption energy for He is 0.13 eV, for Ne is 0.14 eV, and for Ar is 0.15 eV. These values agree with the experimental data obtained from the atom-probe FIM.[11]

Although physically it is quite obvious that the dipole binding energy is highest when the gas atom is adsorbed at the apex of a surface atom where the field is at a maximum, we shall calculate f_A for a gas atom approaching the center of three tungsten atoms at the (111) plane. This calculation serves to confirm our intuition, as well as to illustrate some of the interesting features. Since the dipole-dipole interaction is extremely short ranged, no appreciable error will be introduced by neglecting the interactions with surface atoms beyond the three closest ones. It can be shown from Eqs. (1) and (2) that in this case

$$f_A = \frac{[1+3(3z^2/d^2-1)\alpha_M/d^3]^2}{[1-9(3z^2/d^2-1)^2\alpha_M\alpha_A/d^6]^2}, \quad (6)$$

where z is the distance between the gas atom and the nuclear plane of the three surface atoms and d is the distance between the gas atom and the metal atoms. Since we are interested in only the relative binding strength with respect to the apex, the polarizability of the (111) atoms is assumed to be also equal to 3.44 Å^3. The results are shown as the broken lines in Fig. 1. It is noted that an equilibrium point exists about 3 Å away from the metal plane. At this distance the gas atom is not in contact with the metal surface yet. According to Earnshaw's theorem of elec-

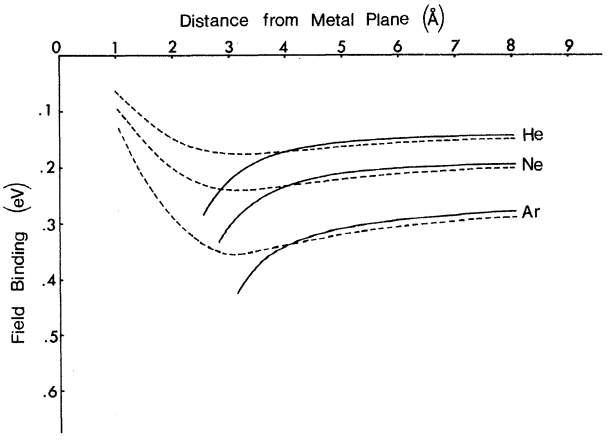

FIG. 1. Field-induced dipole-dipole binding of He, Ne, and Ar on tungsten. Solid lines represent the potential energies of inert-gas atoms when they are directly above a kink-site tungsten atom. Broken lines represent the potential energies when they are above the center of three tungsten atoms with a (111) structure.

trostatics, the equilibrium can only be a saddle point. Since the potential energy is much higher in this case, the gas atom will roll over to the apex of one of the surface atoms and be bound there. At the apex site, the small contribution due to van der Waals forces can be neglected. With this new concept of field adsorption, some of the current views of the field ionization process have to be considerably changed. Several points, which need to be investigated more elaborately, may be mentioned here.

(1) In field ion microscopy an adsorption-free emitter surface is nonexistent. A clean surface can still be obtained by field evaporation in ultrahigh vacuum at low temperatures. However, once the imaging gas is introduced, each of the more protruding surface atoms having a field high enough to cause ionization will be capped by a gas atom. As the adatom remains invisible, the FIM image still represents the atomic surface structure. Adsorption of the imaging gas atom is less probable in the middle of closely packed planes for two reasons. First, the external field F_0 is lower. Second, the polarizability of a surface atom inside a closely packed plane is quite small. We have also considered a repulsive potential between two neighboring adsorbed atoms, which turned out to be only in the negligible order of 0.01 eV.

(2) It is well known that in the presence of an imaging gas, the evaporation field of surface atoms is reduced.[1,9] The reduction depends on emitter material and the kind of imaging gas used.[12] For He the reduction is about 1 to 2%, for Ne about 6%, and for Ar up to 20%. This must be due to the drawing away of part of the electrons bonding the surface atom with the lattice by the inert-gas adsorption. The problem of field evaporation in the presence of the imaging gas is further complicated by the occurrence of multiply charged metal–noble-gas ions some of which may be short lived.[10-12]

(3) Modifications are needed in the theory of field ionization. It appears that ionization occurs when the imaging gas atom "touches" the adatom at the critical distance from the surface. This accounts for the extremely sharp location of the ionization zone which we have found earlier[16] to have a half-width of 0.2 Å. The improved imaging of the low-field regions of a tungsten emitter by the use of a helium-neon mixture[9] may now be seen as being due to apex-site adsorption of neon. With its larger diameter neon extends the critical distance far enough to place the touching helium atom's ground state above the Fermi level where it can be ionized at a reduced field.

Other basic imaging problems in field ion microscopy, such as the invisibility of one atomic species in some alloys,[17] of sectors of (0001) plane edges of hexagonal metals,[18,19] or of sections of biomolecules,[20] may be viewed in a new light by considering the polarizability of these special sites which will control the local adsorption and subsequently the ionization of the imaging gas.

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