

# **Ion-microscopy determination of the energy of intrinsic interstitial atoms**

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A method is proposed for measuring the formation energy of interstitial atoms on the basis of low-temperature field evaporation. The energies of intrinsic interstitial atoms in a metal have been determined by direct experiments for the first time.

Intrinsic point defects are unavoidable structural elements of metals in either an equilibrium or nonequilibrium state. The formation energies  $E_i^f$  and the migration energies  $E_i^m$  of point defects must be known in order to evaluate the rates of structural changes and phase transitions during bombardment, heating, and mechanical treatment. These energies are extremely important parameters in most theories of structure-sensitive properties of solids. Theories of point defects contain numerous approximations and, in general, cannot reliably predict absolute values of the formation energy of interstitial atoms.<sup>1</sup> Experimental methods for determining  $E_i^f$  are based on measurements of characteristics of the metals which depend in a known way on the defect concentration. The number of interstitial atoms at thermodynamic equilibrium, even below the melting point, is small and is not manifested in physical properties against the background of equilibrium vacancies. Accordingly, there have so far been no experimental measurements of the formation energy of intrinsic interstitial atoms.

In this letter we wish to propose an ion-microscopy method for directly determining the energy of an intrinsic interstitial atom,  $E_i^f$ . The method for measuring  $E_i^f$ , like the known method<sup>2,3</sup> for determining the binding energy of atoms,  $\Lambda$ , is based on field evaporation, which is characterized by a strong dependence of the threshold field for evaporation on the total energy of the surface atoms. The energy  $E_i^f$  is defined as the energy of the penetration of a surface atom into the crystal. It is usually reckoned from the energy level of a surface atom bound to a break in a surface step.<sup>1</sup> Strictly speaking, the energy  $E_i^f$  depends on the particular surface state to which the interstitial atom goes when it leaves the surface: a planar face or some break in a surface step. There is accordingly a set of energies  $E_i^f$ , and the value of  $E_i^f$  found from the concentration of interstitial atoms in thermodynamic experiments [in accordance with the expression  $c \sim \exp(-E_i^f)/kT$ ] is actually an average formation energy, reckoned from some undetermined level. Under the conditions of an ion-microscopy experiment, there is no uncertainty regarding the meaning of  $E_i^f$ , since the interstitial atoms go into an adsorbed state at a planar face. The formation energy  $E_i^f$  is thus reckoned from the bottom of the adsorption well.

As an interstitial atom migrates toward the surface, its excess energy  $E_i^f$  decreases by an amount equal to the work performed by the image forces, to the level  $E_i$  in the last near-surface interstitial position. This work is on the order of the

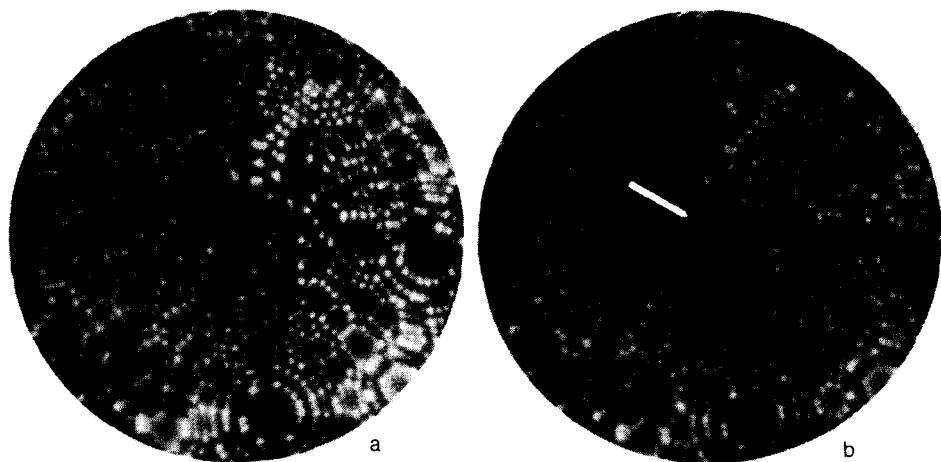


FIG. 1. Ion micrographs of a tungsten sample (a) before and (b) after bombardment with helium atoms. The arrow marks an atom which has emerged at the (110) face.

energy of the migration barriers  $E_i^m$ . Since we have  $E_i^m \ll E_i^f$ , we can assume  $E_i^f \simeq E_i$  (Ref. 4). The theoretical foundation for this method of determining  $E_i$  is the following assumption (which is supported by experiment): After surmounting the last surface barrier, the interstitial atom is in a near-surface adsorption well with the same energy ( $E_i$ ) as before the transition, since it has not managed to transfer this excess energy to the lattice. In other words, it is in a highly excited state in the adsorption well. A certain time later, the atom goes to the adsorption ground state in the course of a relaxation process. Consequently, an electric field can evaporate adsorbed atoms from either the ground state or the highly excited state. Particular features of the evaporation of atoms in the ground state have been analyzed previously to determine the binding energy of surface metal atoms.<sup>2,3</sup> Since the evaporating field depends strongly on the total energy of the evaporated atom, the unknown quantity  $E_i \simeq E_i^f$  can be determined from the difference between the fields in these two cases.

The present experiments were carried out in a two-chamber field ion microscope, equipped with a source of accelerated neutral helium atoms.<sup>5</sup> The test samples were cooled to liquid-hydrogen temperature. The residual gas pressure in the working chamber, measured during the formation of a monolayer of adatoms, did not exceed  $10^{-6}$  Pa. Needle-shaped samples, with a tip radius of curvature of 20–60 nm, were prepared by electrochemical etching from a tungsten wire of 99.98% purity. They were polished by evaporation in an electric field to the point that an atomically smooth surface was formed. The samples were then subjected to an *in situ* bombardment by neutral helium atoms with an energy of 7.0 keV, in a flux of  $(1-15) \times 10^{11}$  atoms/(cm<sup>2</sup> · s). This bombardment was carried out in the direction perpendicular to the [110] axis, which coincided with the axis of the sample. During the bombardment and for 5–20 s after the source was turned off, we measured the diffusive yield of interstitial atoms to a (110) face, which was not bombarded.

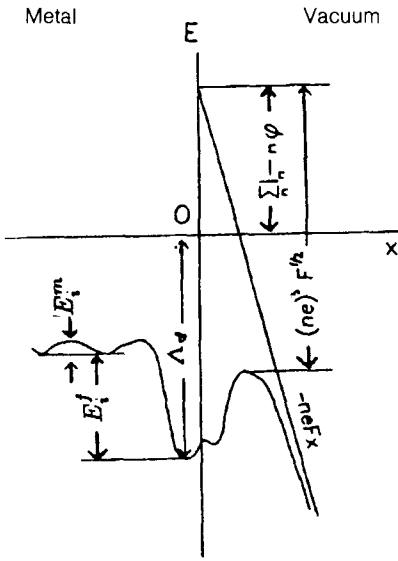


FIG. 2. Energy diagram of the field evaporation of an interstitial atom which has emerged at a surface. The distance  $x$  is reckoned from an effective electron surface.

Figure 1 shows ion micrographs of the surface of the sample (a) before and (b) after bombardment with a flux of  $5 \times 10^{12}$  atoms/cm<sup>2</sup> at a field of  $4.2 \times 10^{10}$  V/m. The field was calculated from the ratio of the working voltage to the threshold voltage for the evaporation of tungsten at 20 K, which corresponds to a field of  $5.8 \times 10^{10}$  V/cm. Interstitial atoms which reached the surface were detected as additional centers of an elevated emission contrast. Our studies showed that the number of atoms which reached the surface and which were detected after the bombardment was strongly dependent on the field applied during the bombardment. As the field was raised from  $4.3 \times 10^{10}$  to  $4.5 \times 10^{10}$  V/m, the number of atoms detected decreased, essentially to zero. At fields below  $4.3 \times 10^{10}$  V/m, the flux of interstitial atoms which was detected was independent of the field and was approximately equal to the flux of atoms, of radiation origin, reaching the surface in the absence of the field.

To remove the intrinsic atoms which reached the surface and became adsorbed on the (110) face, we need substantially stronger electric fields:  $E_d = (5.1 \pm 0.4) \times 10^{10}$  V/m. The difference between desorption fields is evidence that the energy of formation of an interstitial atom which is released strongly influences the field-evaporation process. This effect can be described quantitatively on the basis of a model of image forces.<sup>2</sup> As can be seen from the energy diagram in Fig. 2, the energy of a near-surface interstitial atom lies above the ground state of an intrinsic adatom in a defect-free lattice by an amount  $E_i$ . As a result, the image-force barrier is overcome at comparatively low values of the field,  $F_i$ . It follows directly from the image-force model that the field required to evaporate an atom, activated by the release of an energy  $E_i$ , is

$$F_i = (ne)^{-3} \left( \Lambda_d - E_i + \sum_n J_n - n\phi \right)^2, \quad (1)$$

where  $n$  is the charge number of the evaporated ion,  $\Lambda_d$  is the desorption energy,  $\Sigma_n J_n$  is the total ionization energy, and  $\varphi$  is the work function. Strictly speaking, the quantities  $\Lambda_d$ ,  $E_i$ , and  $\varphi$  depend on the crystallographic orientation and the curvature of the surface region under study. In order to reduce the error, we would thus like to determine  $E_i$  from the difference between the fields  $F_i$  and  $F_d$ , found under the same experimental conditions:

$$E_i = (ne)^{3/2} (F_d^{1/2} - F_i^{1/2}). \quad (2)$$

At low temperatures, tungsten evaporates in the form of triply and quadruply charged ions.<sup>2</sup> At  $F_i$ , both types of ions overcome the barriers. Accordingly, to determine the energy which is released when an interstitial atom reaches the surface, we must assume  $n=4$ , which corresponds to the higher image-force barrier. Substituting the values  $F_d=5.1 \times 10^{10}$  V/m and  $F_i=4.4 \times 10^{10}$  V/m into expression (2), we find the energy of an interstitial atom to be  $E_i=4.7 \pm 0.8$  eV.

Since the literature has no reliable data on the formation energy of interstitial atoms, we calculated  $E_i^f$  by numerical simulation, using a Johnson binary potential.<sup>6</sup> The model crystallite consisted of 840 interacting atoms. The boundary conditions and the calculation procedure are similar to those in Ref. 7. The minimum value of  $E_i^f$  turned out to be 4.9 eV, i.e., in agreement with the value found here for  $E_i$  for tungsten, within the experimental error. This agreement of  $E_i$  and  $E_i^f$  supports the assumption that the work performed by the image forces in moving an interstitial atom from the interior to the surface region is small. It furthermore follows that the atom reaches the surface with an energy close to  $E_i^f$ , i.e., virtually without any energy loss due to the excitation of the lattice. This excess energy is transferred to the lattice when the atom undergoes a transition to the adsorption ground state (or during thermalization).

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<sup>1</sup>A. N. Orlov and Yu. V. Trushin, *Energy of Point Defects in Metals* [in Russian] (Energoatomizdat, Moscow, 1983).

<sup>2</sup>E. W. Müller and T. T. Tsong, *Field Ion Microscopy* (American Elsevier, New York, 1969).

<sup>3</sup>H. J. Mamin *et al.*, *Phys. Rev. Lett.* **65**, 2418 (1990).

<sup>4</sup>V. I. Gerasimenko *et al.*, *Fiz. Tverd. Tela (Leningrad)* **25**, 2456 (1983) [*Sov. Phys. Solid State* **25**, 1410 (1983)].

<sup>5</sup>Zh. I. Dranova *et al.*, *Prib. Tekh. Eksp.*, No. 6, 166 (1980).

<sup>6</sup>R. A. Johnson and P. J. White, *Phys. Rev. B* **18**, 2939 (1978).

<sup>7</sup>V. S. Boiko and T. I. Mazilova, *Fiz. Tverd. Tela (Leningrad)* **34**, 2244 (1992) [*Sov. Phys. Solid State* **34**, 1199 (1992)].

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