Model for Anomalous Self-Diffusion in Group-IV*B* Transition Metals

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A model for anomalous diffusion in the bcc phase of group-IV*B* transition metals is proposed, based on the identity of structure of the activated complex for diffusion and the basal plane of the low-temperature metastable ω phase. An expression for the diffusion coefficient is derived from a phenomenological free energy of formation of an ω embryo. Excellent agreement is obtained with experimental data for bcc Zr.

It is well established that bcc titanium, zirconium, and hafnium along with γ-uranium and the rare earths δ-cerium and β-praseodymium exhibit anomalous diffusional properties.[1-3] Normal behavior is characterized by a diffusion coefficient D given by

$$D = D_0 \exp(-Q/RT),$$

with preexponential factor D_0 of order 0.05 to 5.0 cm^2/sec and activation energy given approximately by $Q = 34T_m$, where T_m is the absolute temperature of melting and where R and T are the gas constant and absolute temperature, respectively. D_0 and Q are approximately temperature independent since a plot of $\ln D$ versus $1/T$ yields a straight line over several decades of D. By contrast, the anomalous metals are characterized by Arrhenius plots with significant curvature which has been interpreted as due to either a temperature variation of the activation energy or the participation of more than one mechanism in bulk diffusion.[1,4]

Numerous attempts have been made to explain anomalous diffusion by means of two or more contributing mechanisms.[1,4,5] This approach invariably encounters two serious difficulties: The fact that anomalous diffusion is confined to a very specific group of metals is not explained; nor can the values of the parameters for the low-temperature mechanism be rationalized, i.e., a preexponential factor which is several orders of magnitude lower than that of normal metals and an activation energy at least half as large as the high-temperature one.[1,4]

The approach which allows for a temperature variation of the activation energy seemed to a few investigators to be a more sensible one.[4,6-8] Such a temperature dependence of Q is made plausible by the existence of a low-temperature phase transition. Indeed, all anomalous metals present allotropic phase transitions; in particular Ti, Zr, Hf, and Pr transform from the bcc phase to the hexagonal-close-packed structure stable at low temperatures, and the stable form of uranium at room temperature is orthorhombic, a distorted hcp structure. In addition, Ti, Zr, and Hf transform to a metastable hexagonal (but not close packed) phase, the so-called ω phase, upon alloying[9] or under pressure.[10] Furthermore, Ti, Zr, Ce, and Hf are group-IV*B* elements, the transition-metal counterparts of group-IV*A* elements, the light elements of which are covalently bonded. The trigonally bonded basal plane of the hexagonal ω structure has, in fact, the structure of the basal plane of graphite indicative of a strong covalent component to the total binding energy.

Thus, the bcc structure appears to be a necessary but not sufficient condition for the diffusional anomalies, the additional condition required being that the bcc structure transform to a hexagonal phase at low temperature. Specifically, Aaronson and Shewmon[6] sought a connection between anomalous self-diffusion and the bcc → hcp transformation while de Fontaine and Buck suggested that the metastable low-temperature ω phase should be responsible for anomalous diffusion.[8]

The present model for anomalous diffusion in Ti, Zr, and Hf is based essentially on the Wert-Zener diffusion theory,[11] while incorporating the essential connection between the atomic jumping process and the tendency for the bcc phase to transform at low temperature to the ω structure. In the Wert-Zener formulation, the diffusion coefficient is expressed as

$$D = \gamma a^2 c_v \Gamma_j, \tag{1}$$

where γ is a numerical constant close to unity, a is the lattice parameter, c_v is the concentration of vacancies at thermal equilibrium with the lattice, and Γ_j is the jump frequency. The problem of calculating D is then reduced to the computation of the jump frequency which, in the case of normal diffusion and in the Wert-Zener approximation, is equivalent to the calculation of the reversible work per mole, ΔG_m, required for an atom to move from an equilibrium position in the lattice to an "activated" configuration from which it can decay spontaneously into a neighboring vacancy. In this idealized jumping process the atom is assumed to vibrate with a constant frequency ν_0, usually taken as the Debye frequency, so that

$$\Gamma_j = \nu_0 \exp(-\Delta G_m/RT). \qquad (2)$$

From Eqs. (1) and (2) a simple Arrhenius relation for the diffusion coefficient versus temperature is obtained which, as mentioned above, is obeyed over a surprisingly wide temperature range for most elements irrespective of crystal structure.

When an atom exchanges places with a nearest-neighbor vacancy in a bcc lattice, it passes through two successive triangular atomic configurations at one third and at two thirds of the jumping distance. It is generally assumed that once the atom has successfully passed the first saddle-point configuration (located at one third) it will overcome the second saddle point and complete the jump with very high probability. The fact that the atom may nevertheless be turned back at the second saddle point introduces a small correction which is easily absorbed in the preexponential parameters of the proposed model. With this in mind, it appears that the key to the explanation of anomalous diffusion consists in recognizing that, in bcc structures, the required activated complex is none other than an ω embryo, that is, the smallest unit or cluster of neighboring atoms having the essential ω-structure characteristics. This can be seen in Fig. 1(a) which shows a (111) plane ABC and an atom at O occupying the normal body-centered site just below the ABC triangle. For this atom to exchange places with a nearest-neighbor vacancy at V, it must first pass through the "activated" position within and at the center of the ABC triangle. This activated configuration is shown in Fig. 1(b), which shows an ω embryo exhibiting elementary "collapse" of two neighboring (111) planes, the one at ABC and the one at O. One recognizes in Fig. 1(b) the characteristic trigonally bonded ω structure.[8] Once the configuration depicted in Fig. 1(b) is reached, the central atom will jump to a nearest-neighbor vacancy, if available, without any extra expenditure in energy as in the case of normal diffusion. The essential difference with normal diffusion comes about when the reversible work of formation of the activated state is calculated. In the case of systems in which the ω structure is a low-temperature metastable phase, close to the transition temperature the free energy of formation of an activated complex (or ω embryo) will be much smaller than in the case of normal bcc metals, resulting in a higher concentration of activated states and consequently enhancing diffusion at low temperatures. On the other hand, in the limit of high temperatures, random thermal vibrations will tend to destroy the ω embryos and the diffusion process should be characterized by normal values and behavior of the diffusion coefficient. Evidence for the existence of ω embryos well above the transition temperature T_0 has been provided recently by neutron[12] and electron[13,14] diffraction.

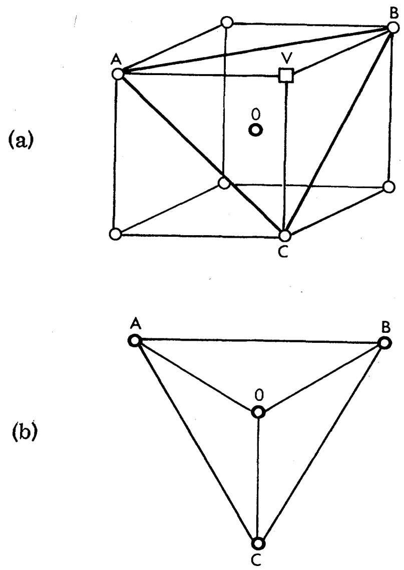

FIG. 1. (a) Body-centered cube showing the $ABC(111)$ plane section, central atom at O, vacancy at V. (b) Activated complex or ω embryo: The atom at O has collapsed into ABC triangle creating trigonal bonds.

By analogy with Eq. (2), the jump frequency Γ_j is then given by

$$\Gamma_j = \nu_0 \exp(-\Delta G_\omega/RT),$$

with ΔG_ω the change in free energy associated with the formulation of 1 mole of activated complex (ω embryos) in thermal equilibrium with the lattice and with ν_0 given approximately by the Debye frequency of the system. The diffusion coefficient is therefore expressed as

$$D=\nu_0\gamma a^2\exp(-\Delta G_\omega/RT)\exp(-\Delta G_v/RT), \qquad (3)$$

where

$$\Delta G_v=\Delta H_v-T\Delta S_v \qquad (4)$$

is the free energy of formation of vacancies, with corresponding enthalpy and entropy.

For a meaningful numerical comparison of the predictions of the present model with experimental results, the relatively involved task of calculating the concentration of activated complexes as a function of temperature should be undertaken. This study is currently under way but, for the sake of illustration, let us merely consider here a simple phenomenological approach to the problem. It is based on an expression for the free energy, first proposed by Cook,[15] which incorporates a strong third-order anharmonic term in some suitably defined short-range order parameter ϵ proportional to the atomic displacements which participate in the formation of an ω embryo. The anharmonic term in the short-range order parameter can be justified, for example, by the omega-antiomega asymmetry pointed out by Cook.[15]

Up to the third order in this order parameter, the phenomenological expression for the change in free energy due to the formation of 1 mole of ω embryos will be

$$\Delta G_\omega=A(T,P)\epsilon^2-B(T,P)\epsilon^3, \qquad (5)$$

where $A(T,P)$ and $B(T,P)$ are unknown functions of temperature and pressure. The value of the coefficient of the anharmonic term, $B(T,P)$, which drives the bcc-to-ω phase transformation, should increase with decreasing temperature and become negligible at high temperatures. A simple temperature dependence of B on T is thus

$$B(T,P)\simeq\alpha/T,$$

where the parameter α will, in general, depend on pressure only.

At very high temperatures, where a normal diffusion mechanism operates, only the harmonic portion of the free energy is significant. Thus one may write

$$\Delta G_\omega(T\gg T_0)\simeq A(T)\epsilon^2 =\Delta G_m=\Delta H_m-T\Delta S_m, \qquad (6)$$

where ΔG_m is the normal activation free energy for vacancy diffusion, ΔH_m and ΔS_m being the corresponding enthalpy and entropy contributions (the latter being quite small).

At the transition temperature, the free energy of formation of ω embryos vanishes so that Eq. (5) may be rewritten as

$$\Delta G_\omega=\Delta G_m(1-T_0/T).$$

By combining the last five equations one obtains for the diffusion coefficient

$$D=D_0\exp(-Q/RT)\exp(\Delta H_mT_0/RT^2), \qquad (7)$$

where

$$D_0=\gamma a^2\nu_0\exp[(\Delta S_m+\Delta S_v)/R]$$

and

$$Q=\Delta H_m+\Delta H_v-T_0\Delta S_m.$$

Equation (7) cannot be strictly valid for temperatures too close to T_0 since a vanishing activation energy for vacancy motion would result at the transition temperature. Actually, although ΔG_ω vanishes at this temperature, a finite activation energy is still required to form even bulk ω since the transition bcc → ω is first order.[15] Thus, at T_0, a roughly temperature-independent residual activation energy for vacancy motion must exist; it is implicity contained in the parameter Q of Eq. (7).

Without the second exponential factor, whose influence at high temperatures is negligible, Eq. (7) is just the classical formula for normal diffusion. We may then estimate Q by use of the empirical rule,

$$Q=34T_m, \qquad (8)$$

alluded to in the first paragraph. Likewise, ΔH_m is a classical quantity whose value should be close to one half of Q.

In the particular case of self-diffusion in bcc Zr, Eq. (8) gives $Q=70$ kcal/mole, and T_0 is estimated to be about 890°K by extrapolation of the ω transition temperature curve versus composition in a Zr-Nb alloy.[16] The remaining two parameters, D_0 and ΔH_m, can be determined by fitting Eq. (7) to the data of Federer and Lundy[17] yielding $D_0=0.21$ cm^2/sec and $\Delta H_m=32.5$ kcal/mole, both parameters falling well within the expected range of values. As can be seen from Fig. 2, the fit is as perfect as the data warrant.

The proposed theoretical model is simple, the resulting Eq. (7) for the diffusion coefficient has direct physical meaning, all parameters used

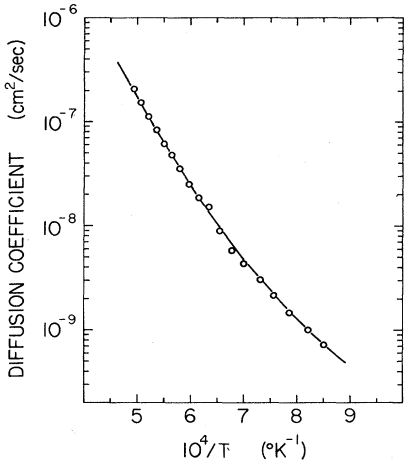

FIG. 2. Arrhenius plot for self-diffusion in Zr. Open circles are data of Federer and Lundy (Ref. 16); solid line represnets the fitted equation (5).

have the expected magnitudes, and the fit to available data is as close as can be. Although the present model applies strictly to Ti, Zr, and Hf, where the metastable ω phase has been reported, the authors believe that a similar mechanism should apply to the other anomalous bcc metals, the only requirement being the tendency to form trigonal bonds on a (111) plane, as in the ω structure. Further work, both theoretical and experimental, is needed to elucidate this point. A cluster-variation study of the temperature dependence of the concentration of ω embryos above T_0 is in progress.

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X-Ray-Diffraction Studies of Acoustoelectrically Amplified Phonon Beams*

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Highly resolved satellite peaks due to acoustoelectrically amplified phonons are observed on the wings of double-crystal x-ray diffraction peaks in InSb single crystals. The frequencies of the observed phonon peaks range between 0.9 and 6.3 GHz, depending on carrier concentration. Second- and third-order satellites are also visible in all profiles, showing the generation of second and third harmonics of the fundamental frequencies of the amplified phonons and, possibly, the existence of multiphonon scattering.

An intense field of quasi monochromatic acoustic phonons with well-defined directions of propagation and polarization can be produced in piezoelectric semiconductors by acoustoelectric (AE) amplification of phonons from the thermal-equilibrium background. The characteristics[1,2] of such amplified phonon beams at frequencies below ≈ 5 GHz have been analyzed intensively in