

Pressure-induced thermodynamic properties of atom-vacancy solid solution

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The thermodynamic properties (TP) of atom-vacancy solid solutions are investigated with molecular-dynamics calculations using N -body potentials. For the example of copper we analyze the vacancy concentration dependence of TP in the high-pressure simulations. Calculated pressure-induced TP of atom-vacancy solid solutions in copper prove the necessity of accounting the peculiarities of the crystal structure and potential in the study of vacancy-driven properties of solids. [S0163-1829(96)00234-2]

The high-pressure properties of solids have been the subject of a vast amount of attention over the past 40 years. Usually the research on the influence of high pressures is focused on the study of dynamic and static properties of solids. The description of pressure-induced behavior is complicated by phase formation. This is the reason why high-pressure study traditionally converges to the investigation of the conditions of formation and stability of phases under pressure (see, for example Refs. 1 and 2).

It is well-known that the existence of vacancy-type defects (VTD's) plays an important role in mechanical, optical, and electrical properties of solids. VTD's mostly define diffusion and phase transformations in solids. Some recent papers^{3,4} prove the vacancy-driven phase transitions as a mechanism of the martensite transformation. Study of VTD properties under pressure may therefore be an important point in the understanding of the high-pressure behavior of solids.⁵⁻⁷

The development of the theoretical study of VTD-induced properties is limited by the need to consider solids with a very low concentration of VTD's. A typical value of the VTD concentration in d metals is about $10^{-3} - 10^{-5}$ (Ref. 8) and in semiconductors it is even less ($\sim 10^{-8} - 10^{-10}$).⁹ Thus the number of atoms that have to be taken into account in cluster or supercell calculations for metals should be $10^3 - 10^5$. Nevertheless, the size of the supercell may be determined from the range over which VTD's can effectively interact with each other. This is not directly related to the equilibrium concentration of VTD's, which is a function of temperature and formation energy through the Boltzmann distribution. There should be some VTD-VTD separation distance beyond which VTD interactions are negligible and a relationship between vacancy formation energies and concentrations no longer exists. In this case the effective interaction radius, ρ_0 , is the physical parameter which determines the size of calculation required to evaluate a VTD formation energy which is comparable with the experimental data.^{10,11} Theoretical evidence of the existence of the physical parameter ρ_0 is given by calculations for Al,¹⁰ which shows almost

no variation in the formation energy for a change of the supercell size from 8 to 32 atoms. The results of Ref. 10 indicate that this situation exists at quite high concentrations of vacancies in Al. Even though the VTD concentrations in this case are high and very far from reality, the obtained values are in a reasonable agreement with the measured data. For metals ρ_0 may be small due to the effective screening of the charge variations by the almost free-electron gas, although for semiconductors ρ_0 is larger due to the long-range character of interatomic interactions.

To describe thermodynamic properties (TP's) of atom-vacancy solid solutions under pressure we have to use methods of statistical physics and to take into consideration a crystal structure. That is the reason why in calculations of the thermodynamic parameters for vacancies the molecular-dynamics (MD) or Monte-Carlo (MC) methods are widely used (see, for example, Refs. 3 and 4). The main input to MD or MC simulations is the interatomic potentials. The necessity to calculate the relaxation of the lattice for metals leads to the inclusion of volume-dependent terms in the interatomic potentials. The account of these many-atomic terms is very important for the correct calculation of vacancy formation energy or relaxations of the lattice in the vicinity of the "empty" site of the crystal lattice. This statement follows immediately from the Cauchy relation, which is automatically satisfied for pairwise interactions and fails in metallic systems. The same concerns the study of the behavior of the metal with vacancies under pressure in MD or MC simulations. Introducing nonpairwise interaction in metals as will be shown leads to a nonlinear dependence on pressure of thermodynamic properties in an atom-vacancy solid solution.

In order to evaluate the equilibrium concentration of VTD's under pressure we shall start with the representation of the atom-VTD solid solution, assuming it to be of the substitutional type. In the alloy with small concentration of one component it is possible to assume an existence of a disordered solid solution. The concentration of the vacancies is very small ($c_v \sim 10^{-3} - 10^{-5}$) and the disappearance of

the ordering state immediately leads to the statement (see Ref. 12) that the Gibbs free energy of this solution may be written in the following form:

$$\mathcal{G} = E(c_v) + kT[c_v \ln(c_v) + (1 - c_v) \ln(1 - c_v)] + p\Omega, \quad (1)$$

where Ω is the atomic volume corresponding to the concentration of vacancies c_v and to external pressure p . $E(c_v)$ in the unrelaxed pairwise interaction approximation is discussed in detail in Ref. 12. When many-body interactions are accounted for $E(c_v)$ may be written as follows:

$$E(c_v) = {}^*V c_v^2 + (2V_{av} - V_{aa})c_v + V_{aa} + E_{\text{mb}}(c_v), \quad (2)$$

$${}^*V = \frac{1}{2} \sum_{\vec{r}, \vec{r}'} V_{vv}(\vec{r}, \vec{r}'), \quad (3)$$

$$V_{aa} = \frac{1}{2} \sum_{\vec{r}, \vec{r}'} V_{aa}(\vec{r}, \vec{r}'),$$

$$V_{va} = \frac{1}{2} \sum_{\vec{r}, \vec{r}'} V_{va}(\vec{r}, \vec{r}').$$

Here $V_{vv}(\vec{r}, \vec{r}')$, $V_{aa}(\vec{r}, \vec{r}')$, $V_{va}(\vec{r}, \vec{r}')$ are the pairwise interaction potentials between two vacancies, between two atoms, and between an atom and a vacancy, respectively.¹² Summation is done over vectors \vec{r} and \vec{r}' , which link lattice sites of the parent lattice (fcc in the case of copper). $E_{\text{mb}}(c_v)$ is the term which contains many-body interactions and is, in principle, concentration dependent. Using Eq. (1) and the equilibrium condition $\partial \mathcal{G} / \partial c_v = 0$ one immediately gets

$$c_v = \left[1 + \exp\left(\frac{d\mathcal{H}}{dc_v} \frac{1}{kT}\right) \right]^{-1}. \quad (4)$$

\mathcal{H} is the enthalpy and $\mathcal{H} = E(c_v) + p\Omega(c_v)$. This expression is more general than the Boltzman distribution

$$c_v \sim \exp\left(-\frac{\mathcal{H}_v}{kT}\right), \quad (5)$$

which is usually used to describe the temperature dependence of the vacancy concentration. Equation (4) may be reduced to Eq. (5) if one makes a linear approximation for the concentration dependence of \mathcal{H} ,

$$\mathcal{H}(c_v) = \mathcal{H}_0 + c_v \mathcal{H}_v, \quad (6)$$

with \mathcal{H}_v independent of c_v and $\mathcal{H}_v \gg kT$. Equation (4) is a Fermi-type distribution function of vacancies in a completely disordered atom-vacancy solid solution. Making use of Eq. (2), Eq. (4) may be rewritten as follows:

$$c_v = \left(1 + \exp\left\{ \left[\left(2{}^*V + \frac{\partial^2 E_{\text{mb}}}{\partial c_v^2} \right) c_v - V_{aa} + 2V_{va} + \frac{\partial E_{\text{mb}}}{\partial c_v} + p \frac{d\Omega}{dc_v} \right] \frac{1}{kT} \right\} \right)^{-1}. \quad (7)$$

It is customary to suggest that at some pressure p

$$\Omega = \Omega_a^p + \Omega_v^p \frac{c_v}{1 - c_v} - {}^*\Omega c_v, \quad (8)$$

here Ω_a^p is an atomic volume, Ω_v^p is a vacancy formation volume, and ${}^*\Omega$ is a measure of the deviation of Ω from Zen's law. Let us turn to Eq. (6) which is usually treated as the definition of the formation energy of vacancies. It may be considered as the first term of a polynomial function:

$$\mathcal{H}(c_v) = \mathcal{H}_0 + c_v \mathcal{H}_v^{(0)} + \frac{1}{2} c_v^2 \mathcal{H}_v^{(1)} + \dots \quad (9)$$

Here $\mathcal{H}_v^{(0)}$ and $\mathcal{H}_v^{(1)}$ are the expansion coefficients. Introducing the square term allows us to get the concentration-dependent formation enthalpy of vacancies:

$$\mathcal{H}_v = \frac{d\mathcal{H}}{dc_v} = \mathcal{H}_v^{(0)} + c_v \mathcal{H}_v^{(1)} + \dots \quad (10)$$

Confining the powers to the first two terms of Eq. (10) we obtain

$$\mathcal{H}_v^{(0)} = -V_{aa} + 2V_{av} + p(\Omega_v^p - \Omega_a^p) + \frac{\partial E_{\text{mb}}}{\partial c_v}, \quad (11)$$

and

$$\mathcal{H}_v^{(1)} = 2({}^*V + {}^*\Omega p) + \frac{\partial^2 E_{\text{mb}}}{\partial c_v^2}. \quad (12)$$

Expression (12) gives a physical meaning of the additional term $1/2 \mathcal{H}_v^{(1)} c_v^2$ which is determined by the mixing energy in the pairwise interaction approximation, the mixing volume in atom-vacancy solid solution, and by the second derivative of the many-body term on concentration of vacancies. Here we assume that ${}^*\Omega$ is a pressure-independent term and so there are only two pressure-dependent contributions to the averaged atomic volume Ω . The term including $\mathcal{H}_v^{(1)}$ is linked with the mixing enthalpy of solid solutions, which in the model of a regular solid solution is represented as

$$\Delta \mathcal{H} = Uc(1 - c). \quad (13)$$

Comparing the term proportional to c^2 with the corresponding term proportional to c_v^2 from Eq. (9) we find

$$\mathcal{H}_v^{(1)} = -2U. \quad (14)$$

Thus U should consist of two terms: one is the energy of vacancy-vacancy pairwise interactions and the second is proportional to $\partial^2 E_{\text{mb}} / \partial c_v^2$ and is the nonlinear change of many-body interactions in atom-VTD solid solution.

To obtain detailed information on the pressure dependence of TP of atom-vacancy solid solutions we have performed molecular-dynamics (MD) simulations for copper, using a cell with 256 atoms. Constant pressure, periodic boundary conditions were used in the evaluation of the enthalpy of the ideal lattice, \mathcal{H}_{256} , and of the cell with a vacancy, \mathcal{H}_{255} . The enthalpy of vacancy formation was calculated for different pressures according to the standard definition:

$$\mathcal{H}_v^f = \mathcal{H}_{N-1} - \frac{N-1}{N} \mathcal{H}_N, \quad (15)$$

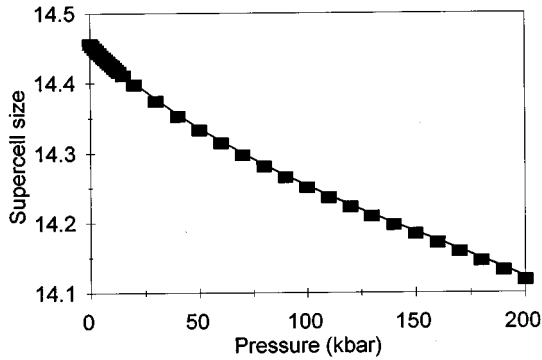


FIG. 1. The pressure dependence of the 256-atom supercell size (\AA) with (solid line) and without (squares) vacancy for copper from the N -body potential MD simulations.

where N is the number of atoms in a supercell, \mathcal{H}_{N-1} and \mathcal{H}_N are the total enthalpies of all the atoms in supercells with the vacancy and without it, respectively.

We allow the simulation to relax the positions of the ions around the vacancy at any fixed value of pressure. We would like to emphasize that this is an essential feature of the MD technique, which enables us to determine the relaxed positions of individual atoms. We used for our calculations the N -body potential for Cu from Ref. 13. The value of the formation volume for a vacancy in Cu was calculated just as shown by Eq. 15. We got the value of formation volume for pressure equal to zero $\Omega_f = 8.3 \text{ \AA}^3$. This result is in good agreement with the experimental results for Cu, $\Omega_f = 0.8\Omega$, where Ω is a volume per atom for an ideal crystal (see Refs. 15) which for Cu is $\Omega = 11 \text{ \AA}^3$. The obtained agreement with experimental results and the tests on system size in Refs. 13 and 14 show that in the N -body potential description the effective interaction radius for vacancies in copper is less than 14.46 \AA , which is the size of the supercell for 256 atoms at zero pressure. The use of N -body potentials in the MD study of the pressure-induced VTD properties is important due to the tight-binding character of N -body potentials: pair potentials give the same value for vacancy formation energy as for cohesive energy, while experiments show these quantities to be different by a factor of 3.

Further, fixing c_v , we proceed to study the pressure-induced TP on the example of copper in the assumption of $\mathcal{H}_v^{(1)} = \text{const}$. This assumption means that our simulations are devoted to the study of the crystal potential response on the TP of atom-vacancy solid solution under pressure. Figure 1 shows the results of the modeling of the pressure dependence of the supercell size. We carried out our calculations for Cu in a fcc lattice. The curvature of the equation-of-state curve of the ideal crystal structure is somewhat different from that of the lattice with the vacancy concentration 3.9×10^{-3} . Such a concentration corresponds to the existence of one vacancy per 256 atomic supercell. We note that the $p(\Omega)$ dependence in our calculations is not linear and that the compressibility of Cu with vacancies is slightly higher.

The behavior of the energy of vacancy formation calculated according to Eq. (15) is plotted in Fig. 2. The formation energy is characterized by the strong nonlinear growth of its value with the growth of pressure. This result has encouraged the additional detailed study of the properties of vacan-

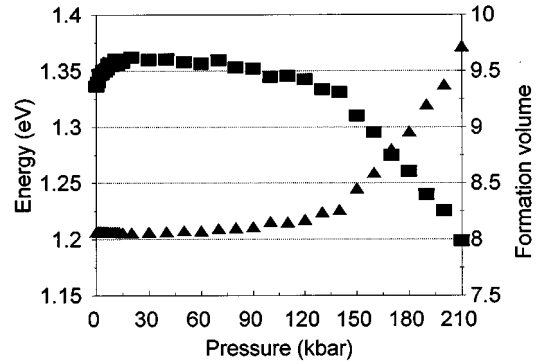


FIG. 2. The vacancy formation energy (triangles), and the vacancy formation volume in \AA^3 (squares) calculated for different pressures for copper with the N -body potential-MD simulations on 256-atom supercell.

cies in a wide pressure region. The dependence of the vacancy formation volume, Ω_f , vs pressure is also shown in Fig. 2. We conclude that Ω_f for copper increases slightly at low pressures (up to 20 kbar) and after that starts to decrease significantly above $p = 150$ kbar. The explanation of the obtained phenomena is presented in Fig. 3. Understanding that Ω_f is the difference of the atomic volume and the relaxation volume we have plotted together with the curve of Ω_f vs p the relaxation volume and the atomic volume dependences. The relaxation volume strongly decreases at small pressures and has the opposite dependence to the vacancy formation volume. Due to the rapid decrease of the relaxation volume in comparison with the rate of decrease of atomic volume the effect of growth of Ω_f is obtained. In the high-pressure region the calculations show the rapid growth of the relaxation volume that leads to the decreasing of Ω_f . This growth of the relaxation volume reflects the significant weakening of the bonds in the high-pressure region. This surprising response to applied pressure may be related to the ‘‘Poisson contraction’’ effect of the $\langle 001 \rangle$ dumbbell copper self-interstitial. In that case a uniaxial tensile strain along $\langle 001 \rangle$ reduces the separation between the dumbbell atoms.¹⁴

In Fig. 4 we have plotted the difference between the ideal (Arrhenius) and nonideal dependences of vacancy concentra-

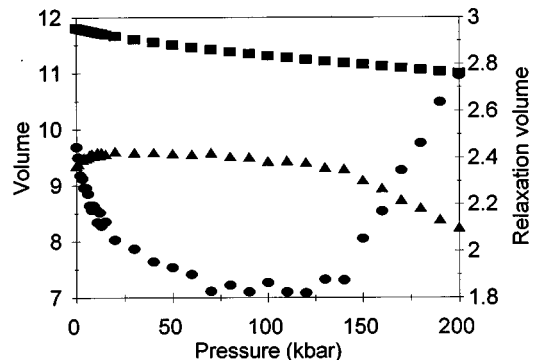


FIG. 3. The equation of states (solid squares) plotted together with the pressure dependence of the relaxation volume in \AA^3 (solid circles) and the vacancy formation volume in \AA^3 (triangles) as a result of the same MD simulations on 256-atom supercell.

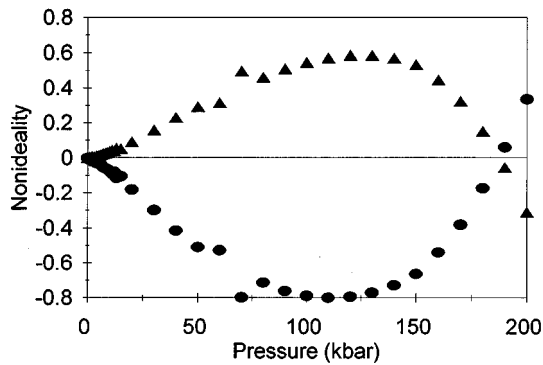


FIG. 4. The difference of logarithms of vacancy concentrations for Arrhenius and non-Arrhenius dependences on pressure (solid circles) and the ratio of this value to a logarithm of a vacancy concentration for an Arrhenius dependence on pressure (solid triangles). The non-Arrhenius dependence was calculated from the 256-cite supercell MD simulations with N -body copper potential at room temperature.

tions. An Arrhenius-type dependence implies a pressure-independent vacancy formation energy. A difference of logarithms of concentrations of 0.3 leads to a decreasing of vacancy concentrations by a factor of 1.3.

The results of the MD simulations on the example of copper in the constant $\mathcal{H}_v^{(1)}$ approximation shows clearly the nonlinear behavior of the pressure-induced TP of the atom–

VTD solid solution even if we neglect V_{vv} and V_{va} contributions. Such simulations show the influence of the crystal potential on the calculations of vacancy properties under pressure. The influence on TP of an atom-vacancy solid solution of a metal lattice with vacancies is actually a consequence of the nontrivial response of the relaxations to the applied pressure. It comes from two factors: (i) the interaction of vacancies, even when their concentration is small; (ii) the nonpairwise character of interatomic forces in metals.

The dependence of the vacancy formation energy and volume on pressure has to be obtained from experimental study of processes where vacancies play a key role. In particular this concerns the study of the pressure behavior of the diffusivity D . Usually such experiments are aimed at obtaining a knowledge about the formation volume. This volume is obtained from the slope of $\partial \ln D / \partial p$ on pressure. However, our simulations have shown that this slope will be different for different pressures. Thus more delicate analysis of experimental data in this case is needed to account the deviations from the straight line in $\partial \ln D / \partial p$ as a function of pressure. The extraction of the data on formation volume for Cu, for example, as shown in our simulations (see Fig. 3), may be performed only in the pressure region 25–75 kbar. In this region the vacancy formation volume Ω_f may be assumed to be pressure independent.

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