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Crystal ordering by structural defects

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Based on calculations of activation process parameters for gold, it is shown that if the energy required to create a defect (vacancy or diffusing atom) is less than a certain value ($h_i < h_{si}$), or the resulting defect has a volume less than a certain value ($v_i < v_{si}$), then this defect has negative entropy, i.e. this defect orders the crystal. The changes in the functions of h_{si} and v_{si} with increasing pressure has been studied.

Keywords: vacancy, self-diffusion, entropy, enthalpy, ordering, gold.

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Formation of crystal defects (vacancies and diffusing atoms) is one of the puzzling phenomena of nature. Why do defects occur in the crystal during isobaric heating or isothermal extension? Do defects always introduce disorder in the thermodynamically stable crystal? These issues require comprehensive investigation. Therefore, investigation of crystal defects attracts a great attention [1–4].

In paper [5] we have proposed an analytical (i.e. free of computer simulation) method for calculating parameters of electrically neutral vacancies formation and atoms self−diffusion in a single−component crystal. In the present work, this method is used to study the correlation of the activation process entropy with enthalpy and volume at different temperatures (T) and pressures (P).

Let us represent a single−component crystal of N atoms as a structure consisting of $N + N_v$ equal−size cells, where N_v cells are vacant and uniformly distributed over the crystal volume V. We assume that atoms in this system may be in two states: localized and delocalized. The localized atom stays in a cell formed by the nearest neighbors and has only vibrational degrees of freedom. The delocalized atom has access to the entire system volume and possesses only translational degrees of freedom.

Assume that the atom can leave the cell if its vibration amplitude within the cell exceeds $c_o/2$, where $c_o = [6k_pV/(\pi N)]^{1/3}$ is the distance between the centers of nearest cells in the initial (not relaxed to the vacancy−activated state) vacancy−free ($N_v = 0$) virtual lattice (indicated by index "o"). Here k_p is the packing index of a structure consisting of $N + N_v$ spherical cells. Thus, the following relation was obtained for the vacancy detection probability [5]:

$$\phi_v = \frac{N_v}{N + N_v} = 1 - \mathrm{erf}\left[\left(\frac{E_v}{k_B T}\right)^{1/2}\right], \tag{1}$$

where k_B is the Boltzmann constant, the probability integral has the following form:

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-t^2)dt, \tag{2}$$

and the vacant cell formation energy in the vacancy−free lattice is defined as follows [5]:

$$E_v = \frac{m}{k_n^o}\left(\frac{3c_o k_B \Theta_o}{8\hbar}\right)^2 f_y\left(\frac{3\Theta_o}{4T}\right). \tag{3}$$

Here $\hbar$ is the Planck constant, m is the atomic mass, k_n^o is the number of all the cells (both occupied and non−occupied) nearest to the given atom, Θ_o is the Debye temperature in the vacancy−free lattice (this is why index "o" is used), function $f_y(y_w)$ appears as follows:

$$f_y(y_w) = \frac{2}{y_w}\frac{[1 - \exp(-y_w)]}{[1 + \exp(-y_w)]}, \quad y_w = \frac{3\Theta_o}{4T}. \tag{4}$$

Let us define the probability of the atom delocalization as a relative fraction of excited atoms whose kinetic energy is higher than threshold energy E_d that is the energy of atom delocalization in the crystal bulk:

$$x_d = \frac{N_d}{N} = \frac{2}{\pi^{1/2}} \int_{E_d/(k_B T)}^{\infty} t^{1/2}\exp(-t)dt$$
$$= 2\left(\frac{E_d}{\pi k_B T}\right)^{1/2} \exp\left(-\frac{E_d}{k_B T}\right) + 1 - \mathrm{erf}\left[\left(\frac{E_d}{k_B T}\right)^{1/2}\right]. \tag{5}$$

The atom delocalization energy is related to the vacant cell formation energy as follows:

$$E_d = \left(\frac{3}{8\pi^2}\right) m \left(\frac{3c_o k_B \Theta_o}{4\hbar k_p^{1/3}}\right)^2 f_y(y_w) = C_{ld}E_v, \tag{6}$$

where the following structural parameter is introduced:

$$C_{ld} = 3k_n^{\mathrm{o}}/(2\pi^2 k_p^{2/3}) > 1.$$

In work [5], we have obtained expressions for the Gibbs energy (g_i), enthalpy (h_i), entropy (s_i) and volume (v_i) for both the formation of the electrically neutral vacancy $(i = v)$ and self–diffusion of atom $(i = d)$ over the crystal volume. When $E_v \gg k_{\mathrm{B}}T$ (which remains valid in metals up to the melting point), these formulae look like for vacancy formation

$$g_v = -k_{\mathrm{B}}T\ln(\phi_v) = E_v\left[1 + \left(\frac{k_{\mathrm{B}}T}{2E_v}\right)\ln\left(\frac{\pi E_v}{k_{\mathrm{B}}T}\right)\right],$$

$$h_v = E_v\left\{1 - t_y(y_w) + \alpha_p T\left[(2 - t_y(y_w))\gamma_{\mathrm{o}} - \frac{2}{3}\right]\right\},$$

$$\frac{s_v}{k_{\mathrm{B}}} = \frac{h_v - g_v}{k_{\mathrm{B}}T} = \frac{E_v}{k_{\mathrm{B}}T}\left\{\alpha_p T\left[(2 - t_y(y_w))\gamma_{\mathrm{o}} - \frac{2}{3}\right]\right.$$

$$\left. - t_y(y_w) - \left(\frac{k_{\mathrm{B}}T}{2E_v}\right)\ln\left(\frac{\pi E_v}{k_{\mathrm{B}}T}\right)\right\},$$

$$\frac{v_v}{v_0} = \frac{E_v}{B_T v_0}\left[(2 - t_y(y_w))\gamma_{\mathrm{o}} - \frac{2}{3}\right], \tag{7}$$

for self–diffusion

$$g_d = -k_{\mathrm{B}}T\ln(x_d) = E_d\left[1 - \left(\frac{k_{\mathrm{B}}T}{2E_d}\right)\ln\left(\frac{4E_d}{\pi k_{\mathrm{B}}T}\right)\right],$$

$$h_d = E_d\left\{1 - t_y(y_w) + \alpha_p T\left[(2 - t_y(y_w))\gamma_{\mathrm{o}} - \frac{2}{3}\right]\right\},$$

$$\frac{s_d}{k_{\mathrm{B}}} = \frac{h_d - g_d}{k_{\mathrm{B}}T} = \frac{E_d}{k_{\mathrm{B}}T}\left\{\alpha_p T\left[(2 - t_y(y_w))\gamma_{\mathrm{o}} - \frac{2}{3}\right]\right.$$

$$\left. - t_y(y_w) + \left(\frac{k_{\mathrm{B}}T}{2E_d}\right)\ln\left(\frac{4E_d}{\pi k_{\mathrm{B}}T}\right)\right\},$$

$$\frac{v_d}{v_0} = \frac{E_d}{B_T v_0}\left[(2 - t_y(y_w))\gamma_{\mathrm{o}} - \frac{2}{3}\right]. \tag{8}$$

Here $\alpha_p = (1/V)(\partial V/\partial T)_P$ is the thermal expansion coefficient, $B_T = -V(\partial P/\partial V)_T$ is the isothermal elastic modulus, $\gamma_{\mathrm{o}} = -[\partial\ln(\Theta_{\mathrm{o}})/\partial\ln(V)]_T$ is the first Gruneisen parameter for the vacancy–free crystal, v_0 is the volume per atom at $P = 0$ and $T = 0\,\mathrm{K}$,

$$t_y(y_w) = -\frac{\partial\ln(f_y)}{\partial\ln(y_w)} = 1 - \frac{2y_w\exp(y_w)}{[\exp(2y_w) - 1]}. \tag{9}$$

Let us represent the pair interatomic interaction in the form of the Mie–Lennard-Jones potential defined as

$$\varphi(r) = \frac{D}{b - a}\left[a\left(\frac{r_{\mathrm{o}}}{r}\right)^b - b\left(\frac{r_{\mathrm{o}}}{r}\right)^a\right], \tag{10}$$

where D and r_{o} are the depth and coordinate of the potential minimum, $b > a > 1$ are the numerical parameters.

Then, as shown in [6], the Debye temperature may be defined in the „only nearest neighbors interaction“ approximation as

$$\Theta_{\mathrm{o}}(k_n^{\mathrm{o}}, c_{\mathrm{o}}) = A_w(k_n^{\mathrm{o}}, c_{\mathrm{o}})\xi\left[-1 + \left(1 + \frac{8D}{k_{\mathrm{B}}A_w(k_n^{\mathrm{o}}, c_{\mathrm{o}})\xi^2}\right)^{1/2}\right]. \tag{11}$$

Function $A_w(k_n^{\mathrm{o}}, c_{\mathrm{o}})$ appears due to taking into account the energy of atom „zero vibrations“

$$A_w(k_n^{\mathrm{o}}, c_{\mathrm{o}}) = K_R\frac{5k_n^{\mathrm{o}}ab(b + 1)}{144(b - a)}\left(\frac{r_{\mathrm{o}}}{c_{\mathrm{o}}}\right)^{b+2}, \tag{12}$$

where

$$K_R = \frac{\hbar^2}{k_{\mathrm{B}}r_{\mathrm{o}}^2 m}, \quad \xi = \frac{9}{k_n^{\mathrm{o}}}.$$

Based on potential (10) in the „only nearest neighbors interaction“ approximation, the state equations P and elastic modulus B_T may be expressed as follows [7]:

$$P = \left[\frac{k_n^{\mathrm{o}}}{6}DU'(R) + \frac{9}{4}k_{\mathrm{B}}\Theta_{\mathrm{o}}\gamma_{\mathrm{o}}E_w(y_w)\right]\frac{1}{v}, \tag{13}$$

$$B_T = -v\left(\frac{\partial P}{\partial v}\right)_T = P + \left[\frac{k_n^{\mathrm{o}}}{18}DU''(R)\right.$$

$$\left. + \frac{9}{4}k_{\mathrm{B}}\Theta_{\mathrm{o}}\gamma_{\mathrm{o}}(\gamma_{\mathrm{o}} - q_{\mathrm{o}})E_w(y_w) - 3k_{\mathrm{B}}\gamma_{\mathrm{o}}^2 TF_E(y_w)\right]\frac{1}{v}. \tag{14}$$

Here $v = V/N$, $R = (v_0/v)^{1/3}$ is the relative linear crystal density,

$$E_w(y_w) = 0.5 + \frac{1}{[\exp(y_w) - 1]},$$

$$F_E(y_w) = \frac{y_w^2\exp(y_w)}{[\exp(y_w) - 1]^2}, \quad v_0 = \frac{\pi r_{\mathrm{o}}^3}{6k_p},$$

$$U(R) = \frac{aR^b - bR^a}{b - a}, \quad U'(R) = R\left[\frac{\partial U(R)}{\partial R}\right] = \frac{ab(R^b - R^a)}{b - a},$$

$$U''(R) = R\left[\frac{\partial U'(R)}{\partial R}\right] = \frac{ab(bR^b - aR^a)}{b - a}. \tag{15}$$

It is easy to derive from (11) the following expressions for the first (γ_{o}) and second (q_{o}) Gruneisen parameters for a vacancy–free crystal:

$$\gamma_{\mathrm{o}} = -\left(\frac{\partial\ln\Theta_{\mathrm{o}}}{\partial\ln v}\right)_T = \frac{b + 2}{6(1 + X_w)},$$

$$q_{\mathrm{o}} = \left(\frac{\partial\ln\gamma_{\mathrm{o}}}{\partial\ln v}\right)_T = \gamma_{\mathrm{o}}\frac{X_w(1 + 2X_w)}{1 + X_w}. \tag{16}$$

Here function $X_w = A_w\xi/\Theta_{\mathrm{o}}$ has been introduced.

Since the Debye temperature in formula (11) is independent of temperature during the crystal isochoric heating, the isochoric thermal capacity and isobaric thermal volumetric

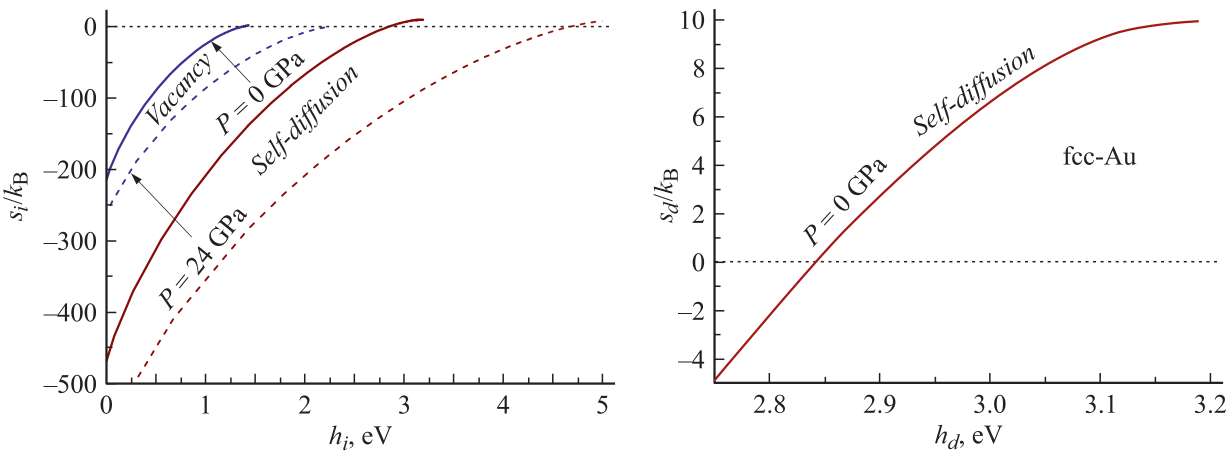

Figure 1. Entropy versus enthalpy in the activation process for gold. Two upper curves relate to the vacancy formation process, two lower curves are for the atom self–diffusion process. Solid lines represent isobars $P = 0$, dashed lines are isobars $P = 24$ GPa. The right graph presents an enlarged view of the $s_d \sim h_d$ dependence in the range where $s_d(T > \Theta_o) > 0$.

expansion coefficient for the vacancy–free crystal may be defined as [8]:

$$C_v = 3Nk_B F_E\left(\frac{3\Theta_o}{4T}\right),$$

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \gamma\frac{C_v}{VB_T} = \frac{\gamma C_v}{NB_T[\pi r_o^3/(6k_p)]}\left(\frac{v_0}{v}\right). \tag{17}$$

In work [5], the temperature dependence of activation process parameters for gold was calculated in the range of $T = 10$ to 1330 K along two isobars: $P = 0$ and 24 GPa. It was shown that at $T < \Theta_o$ the activation parameters strongly depend on temperature due to quantum laws, the activation process entropy being $s_i(T < \Theta_o) < 0$. At $T = 0$ K, the activation process parameters reach their minima: $g_i(0) = 0$, $h_i(0) = 0$, $v_i(0) = 0$, $s_i(0) < 0$. Such a behavior of these functions was shown to agree with the third thermodynamics law in the „strong“ Planck's formulation. Notice that the negative value of the defect formation entropy was revealed in both the experimental [9,10] and theoretical [1,11] works. At $T \gg \Theta_o$, the vacancy detection probability and self–diffusion coefficient transform into the classical Arrhenius dependences with the enthalpy slightly dependent on temperature; here the defect entropy is positive: $s_i(T \gg \Theta_o) > 0$.

As shown in [5], the enthalpy, entropy and volume of the activation process increase with isobaric heating of the crystal. Therefore, they are to correlate with each other. In this work, the following correlations between the activation process parameters were studied: $s_i(T) \sim h_i(T)$ and $s_i(T) \sim v_i(T)$. These correlations were studied based on the performed calculations of Au activation parameters for the temperature range $T = 10$–1330 K along two isobars: $P = 0$ and 24 GPa.

Fig. 1 presents the calculated dependence of activation process entropy on enthalpy $s_i \sim h_i$ along two isobars. Long time ago, experiments performed at high temperatures revealed the following linear dependence:

$$\frac{s_i}{k_B} = Com_i + \frac{h_i}{k_B T_{com(i)}}, \tag{18}$$

where Com_i and $T_{com(i)}$ are empirical fitting parameters.

In literature, dependence (18) was named as „compensation effect“ or „Meyer–Neldel law“ [12]. However, Fig. 1 shows that the $s_i \sim h_i$ dependence may be assumed to be linear only in a narrow temperature range, and „compensation temperature“ $T_{com(i)}$ increases with increasing pressure.

Taking (8) as a basis, it is easy to derive the self–diffusion entropy formula in the following form:

$$\frac{s_d}{k_B} = \frac{E_d}{k_B T}\left\{\alpha_p T\left[(2 - t_y(y_w))\gamma_o - \frac{2}{3}\right] - t_y(y_w)\right\} + \frac{1}{2}\ln\left(\frac{4E_d}{\pi k_B T}\right). \tag{19}$$

For high temperatures ($T \gg \Theta_o$), obtain from (9) $t(y_w \ll 1) \ll 1$. The $\alpha_p T$ value is much lower than unity even at $P = 0$ and melting point (T_m): $\alpha_p T_m \ll 1$. Therefore, based on (8) at $T \gg \Theta_o$ it is possible to assume that $E_d \cong h_d$. This allows transforming (19) to

$$\frac{s_d}{k_B} \cong 2\frac{h_d}{k_B}\alpha_p\left(\gamma_o - \frac{1}{3}\right) + \frac{1}{2}\ln\left(\frac{4h_d}{\pi k_B T}\right). \tag{20}$$

Since in the $T_m > T \gg \Theta_o$ range parameters α_p and γ_o vary slightly with isobarically increasing temperature, and function h_d increases linearly, relation (20) provides easy understanding of the origin of the „compensation effect“ (18).

Fig. 2 presents the calculated dependence of the activation process entropy on volume $s_i \sim v_i$. Linear dependence $s_i/k_B = A_i + Zen_i v_i/v_o$ was revealed in self–diffusion experiments long time ago; it is referred to as „relations of

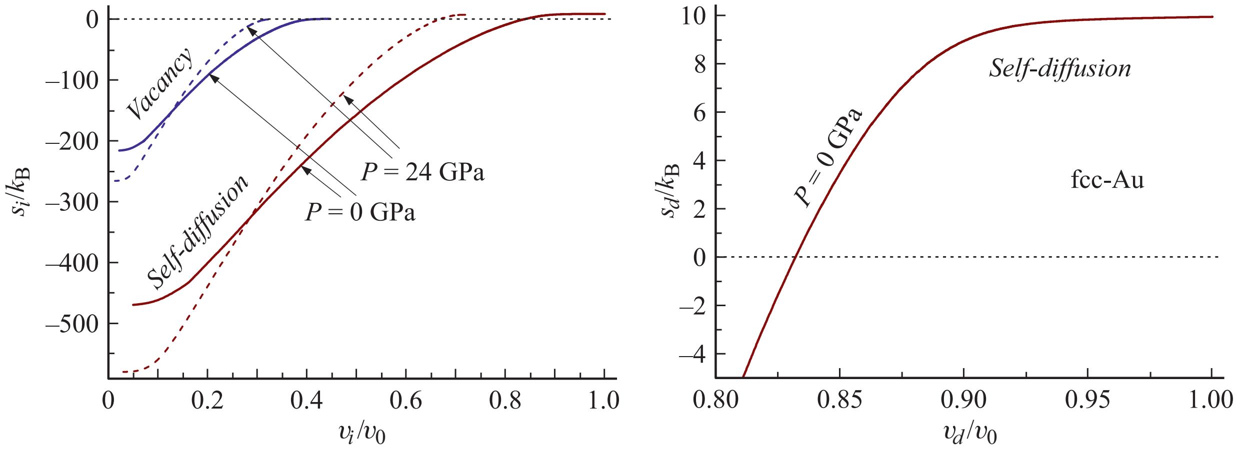

Figure 2. Entropy versus volume in the activation process for gold. Two upper curves relate to the vacancy formation process, two lower curves are for the atom self–diffusion process. Solid lines represent isobars $P = 0$, dashed lines are isobars $P = 24$ GPa. The right graph presents an enlarged view of the $s_d \sim v_d$ dependence in the range where $s_d(T > \Theta_o) > 0$.

Zener–Keyes–Lawson“ [13]. Fig. 2 shows that dependence $s_i \sim v_i$ is linear only in a narrow temperature range, and coefficient Zen_i increases with increasing pressure. Figs. 2 and 3 demonstrate that the following relations are valid: $h_{sd} > h_{sv}$, $v_{sd} > v_{sv}$, $h_{si}(P > 0) > h_{si}(P = 0)$, $v_{si}(P > 0) < v_{si}(P = 0)$, where h_{si} and v_{si} are the enthalpy and volume of the vacancy formation at $s_i = 0$, i. e. vacancies begin disordering the crystal at lower energies or volumes necessary for their creation than the diffusing atoms. Energy necessary for creating a „disordering defect“increases with increasing pressure, while the defect volume required for the crystal disordering decreases.

Conflict of interests

The author declares that he has no conflict of interests.

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