Wavelength dependence of electronic excess energy of a composition-modulated metallic mixture

H. Yamauchi

Department of Engineering Materials, University of Windsor, Windsor, Ontario N9B 3P4, Canada

An electronic excess energy or the difference in electronic energy between the homogeneous metallic solution and one with a composition modulation is calculated by means of the Hohenberg-Kohn formula for the ground-state energy of a nonuniform electron-gas system. Such an electronic excess energy increases as the modulation wavelength decreases and may or may not have a maximum, depending on the system. An effective-gradient-energy coefficient is shown to decrease as the wavelength decreases. This is related to an observation that electron distribution is rather flattened compared with the distribution of positive charges when the wavelength is sufficiently short.

I. INTRODUCTION

Included in Cahn and Hilliard's formula[1,2] for free energy of a nonuniform system were two major contributions: (i) $f(c)$, which depends on the local composition at arbitrary position $\vec{r}, c(\vec{r})$, and (ii) $\kappa(\nabla c)^2$, which is dependent on the composition of the immediate environment through the composition gradient at position $\vec{r}, \nabla c(\vec{r})$ and is termed a "gradient energy" with κ being the gradient-energy coefficient. Utilizing this formula for free energy, Cahn and Hilliard[2] and Cahn,[3] respectively, developed theories of nucleation and of spinodal decomposition.

Recently, we estimated electronic contributions to the mixing energy[4] [which was proportional to the enthalpy term in $f(c)$] and to the gradient energy[5] of a composition-modulated metallic mixture by means of the Hohenberg-Kohn formula for the electronic ground-state energy.[6] In a metallic mixture with a very dilute free-electron density such as an alloy of the Cs-Rb system, a miscibility gap was expected to exist at low temperatures. This was considered as a possible explanation for a continuous solid-solution field below the solidus curve appearing in the experimental phase diagram of such a system as Cs-Rb. Spinodal decomposition was also expected in such a system, though kinetics might be very slow. This was because negative electronic mixing energy and positive electronic gradient energy were expected for a system with a dilute free-electron density, and these contributions were assumed to be dominant in such a system. In mixtures of common metals, these electronic contributions were shown to be merely a part of the total mixing energy and the gradient energy.

In the present work, we employ the same theoretical foundation as the previous ones[4,5] but retain higher-order terms than the gradient-energy term in the electronic excess energy by performing fully numerical calculations. Then the wavelength dependence of the excess energy and an effective gradient energy is discussed.

II. THEORY

A binary mixture of A and B atoms is considered. The local composition in the system is assumed to fluctuate according to a sinusoidal plane wave of the following form:

$$c(x) = c_0 + A \cos(kx) , \tag{1}$$

where $c(x)$ is the local composition of component B on a plane located at position x along the wave-propagation direction, c_0 is the average composition of component B, A is the amplitude of the wave, and k is the wave number, which is equal to $2\pi/\lambda$ with λ being the wavelength. Note that since $c(x)$ is a non-negative quantity, the possible maximum amplitude (which may not be realized by natural spinodal decomposition) is given by

$$A_{\max} = \min(c_0, 1 - c_0) . \tag{2}$$

If ψ_I and v_i represent, respectively, the effective valence number and the atomic volume of an atom of I kind $(I = A, B)$, the density of positive charges may be distributed following

$$n_+(x) = \frac{\psi_A[1 - c(x)] + \psi_B c(x)}{v_A[1 - c(x)] + v_B c(x)} . \tag{3}$$

Here, it must be noted that the discrete nature of the

positive-charge distribution in a crystalline lattice is ignored and positive charges are smeared to yield a continuum, i.e., a jellium model. If both the atomic volume difference between an A and a B atom defined by

$$\epsilon = 2(v_A - v_B)/(v_A + v_B)$$

and the modulation wave amplitude A are small compared with unity, $n_+(x)$ is obtained from Eqs. (1) and (3):

$$n_+(x) = n_0[1 + \alpha \cos(kx)] \ , \tag{4}$$

where

$$n_0 = n_A(1 - c_0) + n_B c_0 + \epsilon(n_A - n_B)c_0(1 - c_0)$$

and

$$\alpha = A(n_B - n_A)[1 - \epsilon(1 - 2c_0)]/n_0 \ ,$$

in which

$$n_I = \psi_I / v_I \quad (I = A, B) \ .$$

Note that n_I represents the average free-electron density of pure metal of I kind, if ψ_I and v_i are not altered by alloying. When $n_+(x)$ obeys a sinusoidal distribution, as given in Eq. (4), it is natural to assume that the electron distribution $n(x)$ follows

$$n(x) = n_0[1 + \beta \cos(kx)] \ , \tag{5}$$

in which the normalized amplitude of electron wave β is a parameter to be determined. It is apparent that $n_+(x)$ and $n(x)$ satisfy the electroneutrality condition within a distance of the wavelength.

According to Hohenberg and Kohn,[6] the ground-state energy U_e of a nonuniform electron-gas system may be given by

$$U_e[n] = E_{es}[n] + T_s[n] + E_x[n] + E_c[n] \tag{6}$$

where E_{es}, T_s, E_x, and E_c are energy functionals of the electron-distribution function n and represent, respectively, the Coulomb, kinetic, exchange, and correlation energy of electrons:

$$E_{es}[n] = \frac{1}{2} \int \int \frac{[n(\vec{r}) - n_+(\vec{r})][n(\vec{r}') - n_+(\vec{r}')]}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \ , \tag{7}$$

$$T_s[n] = \frac{3}{10}(3\pi^2)^{2/3} \int [n(\vec{r})]^{5/2} d\vec{r} + w \int \frac{[\nabla n(\vec{r})]^2}{n(\vec{r})} d\vec{r} \ , \tag{8}$$

$$E_x[n] = -\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3} \int [n(\vec{r})]^{4/3} d\vec{r} \ , \tag{9}$$

and

$$E_c[n] = -\int \{0.0575 + 0.0155 \ln[4\pi n(\vec{r})/3]^{1/3}\} n(\vec{r}) d\vec{r} \ . \tag{10}$$

As has been used in Eqs. (7)—(10), atomic units (a.u.) will be used throughout. As seen in Eq. (8), the Thomas-Fermi—von Weiszacker formula is utilized for the kinetic energy. The second term on the right-hand side of Eq. (8) takes the nonuniformity contribution into account. The von Weiszacker coefficient w may be set equal to $\frac{0.45}{8}$.[7] For the correlation energy, the Nozières-Pines expression [given in Eq. (10)] for an intermediate range of the electron density[8] is employed. In our previous work,[4] the electronic mixing energy was calculated by use of three different expressions for the correlation energy: the Wigner formula for a very dilute electron gas, the Nozières-Pines formula for an intermediate-density electron gas, and the Gell-Mann-Brueckner formula for a very high-density electron gas. The numerical results due to the two former formulas were more or less close. Note that

none of these approximate formulas are sufficiently precise. There may be gradient terms such as the von Weiszacker term even in the exchange and correlation energy.[9] Sometimes, such contributions improved quantitative results.[10] However, they are not taken into account in the present work just for the sake of simplicity. The same choice for T_s, E_x, and E_c as those given in Eqs. (8)—(10) was previously employed by Gyemant and Solt[11] in their study of void formation energy.

With the density distributions of positive charges and of electrons given in Eqs. (4) and (5), respectively, electronic excess energy or the difference in electronic energy per unit volume, $\Delta U_e / V$, between the homogeneous solution [in which $c(\vec{r}) = c_0$] and one with a composition given by Eq. (1) can be calculated by use of Eqs. (6)—(10):

$$\Delta U_e/V = \pi n_0^2 (\alpha - \beta)^2/k^2 + \tfrac{3}{10}(3\pi^2)^{2/3} n_0^{5/3} Q_{5/3}(\beta) - \frac{4}{3}\left[\frac{3}{\pi}\right]^{1/3} n_0^{4/3} Q_{4/3}(\beta)$$

$$- \frac{0.0155}{3} n_0 (\ln\{[1+(1-\beta^2)^{1/2}]/2\} + 1 - (1-\beta^2)^{1/2}) + (\tfrac{0.45}{8}) n_0 [1-(1-\beta^2)^{1/2}]k^2 ,$$

(11)

where the integral $Q_\phi(\beta)$ is defined by

$$Q_\phi(\beta) \equiv \frac{1}{2\pi}\left[\int_{-\pi}^{\pi}(1+\beta\cos\theta)^\phi d\theta - 1\right] = \sum_{m=1}^{\infty} \frac{\phi(\phi-1)\cdots(\phi-2m+1)}{(2m)!}\frac{(2m-1)!!}{(2m)!!}\beta^{2m} .$$

Note that, in the expression of $\Delta U_e/V$ given in Eq. (11), an unknown parameter β is still included. Parameter β should be determined by minimizing $\Delta U_e/V$:

$$d(\Delta U_e/V)/d\beta = 0 = -2\pi n_0^2(\alpha-\beta)/k^2 + \tfrac{1}{2}(3\pi^2)^{2/3} n_0^{5/3} Q_{2/3}(\beta)$$

$$- \left[\frac{3}{\pi}\right]^{1/3} n_0^{4/3} Q_{1/3}(\beta) - \frac{0.0155}{3} n_0 [1-(1-\beta^2)^{1/2}]/\beta + \tfrac{0.45}{8} n_0 \beta k^2/(1-\beta^2)^{1/2} .$$

(12)

III. RESULTS AND DISCUSSION

Utilizing β as a solution of Eq. (12) in Eq. (11), electronic excess energy per unit volume, $\Delta U_e/V$, can be obtained for a given set of parameters n_0, α, and k.

Numerical calculation was performed for solving Eq. (12) by means of the Newton-Raphson method. The numerical integral in Eqs. (11) and (12) were carried out by means of Simpson's rule, applied for every angle section equal to $2\pi/240$. Initial values for β were obtained by approximately solving Eq. (12) for small β's:

$$\beta_{\rm app} = \alpha/[1+(\omega_0/\omega_{es})k^2+(\omega_1/\omega_{es})k^4] ,$$

(13)

where

$$\omega_{es} = \pi n_0^2 ,$$

$$\omega_0 = \tfrac{1}{12}[(3\pi^2)^{2/3} n_0^{5/3} - (3/\pi)^{1/3} n_0^{4/3} - 0.0155 n_0] ,$$

and

$$\omega_1 = \frac{0.45}{16} n_0 .$$

For various values of n_0 and k, numerical results were in excellent agreement with $\beta_{\rm app}$'s given in Eq. (13) within $\pm 1\%$ (but usually within $\pm 0.1\%$). It is easily seen from Eq. (13) that, since ω_{es} and ω_1 are positive quantities, $0 < \beta \leq \alpha$ for any k's if $\omega_0 > 0$. Even for Cs$-\nu$ at.% Rb ($\nu < 60$) alloys in which $\omega_0 < 0$,[4] β's do not exceed α more than 0.1%. In Fig. 1, curve a shows the change of the ratio β/α with respect to the wavelength λ ($=2\pi/k$) in the Cs-50 at.% Rb alloy. It is seen that for $\lambda \lesssim 2$ nm β/α sharply decreases as λ decreases. This is a common feature to almost all alloys, including the Au-50 at.% Ni alloy as demonstrated by curve b.

This indicates that, when composition wavelength λ is larger than $2\sim3$ nm, the electron distribution n varies almost exactly the same as the positive-charge distribution n_+, while n tends to flatten for short λ's. In the cases shown in Fig. 1, β was less than 60% of α at the shortest wavelength λ_m (that was set equal to the lattice constant of the crystal of pure element of smaller size). That is, for $\lambda < 2\sim3$ nm, a series of dipoles, each having a length equal to $\lambda/2$, starts to form. This reminds us of the effective surface energy versus radius curve for spherical voids in metals.[11,12] Owing to the nature of a flattened electron distribution, the effective surface energy of a single atom vacancy in pure Na crystal was reduced to less than 60% of the surface energy of a flat surface.[12]

Figure 2 shows the wavelength dependence of the excess energy in the Cs-50 at.% Rb alloy when the composition wave amplitude is set equal to $A_{\rm max}$ given in Eq. (2). At $\lambda = \infty$ or $k = 0$, $\Delta U_e/(VA^2)$ corresponds to the mixing energy which is negative for this alloy.[4] Since $|\Delta U_e/V|$ at $\lambda = \infty$ is small, $\Delta U_e/V$ becomes positive for λ smaller than 3.7 nm because of a positive gradient energy,[5] and rapidly increases as λ decreases towards λ_m. In our previous works,[4,5] $\beta_{\rm app}$ obtained from Eq. (13) was directly substituted into Eq. (11) to obtain an approximate expression for $\Delta U_e/V$:

$$(\Delta U_e/V)_{\rm app} = \frac{\alpha^2(\omega_0+\omega_1 k^2)}{1+(\omega_0/\omega_{es})k^2+(\omega_1/\omega_{es})k^4} .$$

(14)

Comparison of the numerical values for $\Delta U_e/V$ with $(\Delta U_e/V)_{\rm app}$ shows that both quantities are in agreement within $\pm 4\%$ at any wavelength throughout the Cs-Rb system. (In the Au-Ni sys-
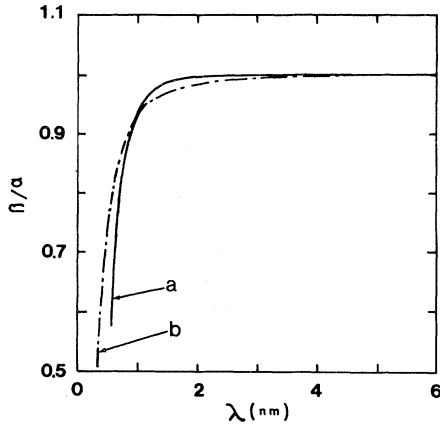
FIG. 1. Wavelength λ dependence of ratio of electron-distribution wave amplitude β [defined in Eq. (5)], to positive-charge distribution wave amplitude α [defined in Eq. (4)] in (a) Cs—50 at. % Rb and (b) Au—50 at. % Ni.
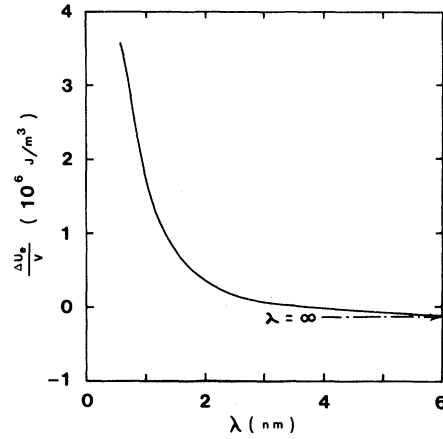

FIG. 2. Wavelength λ dependence of electronic excess energy $\Delta U_e/V$ [defined in Eq. (11)] in Cs—50 at. % Rb when the maximum amplitude [defined in Eq. (2)] is utilized.

tem, the agreement was within ±1%.) Thus, the above comparison ensures the validity of the approximate formula of $\Delta U_e/V$ given in Eq. (14) which was already intensively utilized in previous works.[4,5] It must be noted that if λ becomes smaller than λ_m, $\Delta U_e/V$ approaches zero as can easily be seen from Eq. (14). That is, when $\lambda=0$, the mixture becomes homogeneous in the present continuum model.

If terms of order higher than k^2 are ignored in $\Delta U_e/V$ in order to obtain an analogous expression to Cahn's excess free energy [Eq. (4) of Ref. 3], Eq. (14) may be simplified[4,5] as

$$(\Delta U_e/V)_{\text{app}} = (A^2/4)(u_0'' + 2\kappa_e k^2) , \quad (15)$$

where

$$u_0'' = 4\xi\omega_0 \quad (16)$$

and

$$\kappa_e = 2\xi(\omega_1 - \omega_0^2/\omega_{es}) , \quad (17)$$

in which

$$\xi = \{(n_A - n_B)[1 - \epsilon(1 - 2c_0)]/n_0\}^2 .$$

Since $u_0''A^2/4 = (\Delta U_e/V)_{k=0}$, an effective gradient-energy coefficient may be defined for the excess energy $\Delta U_e/V$ given in Eq. (11):

$$\kappa_{\text{eff}} \equiv 2[\Delta U_e/V - (\Delta U_e/V)_{k=0}]/A^2k^2 . \quad (18)$$

In Fig. 3, κ_{eff} calculated for the Cs—50 at. % Rb alloy is plotted against the wavelength λ. For large λ's, κ_{eff} is nearly constant, being closely equal to κ_e

calculated by use of Eq. (17). However, for small λ's (≤ 1.5 nm), κ_{eff} becomes significantly smaller than κ_e. At λ_m, κ_{eff} is less than 50% of κ_e. Qualitatively speaking, experimentally determined gradient-energy coefficient in such a system as Al-Ag (Ref. 13) seems to reduce its magnitude as the modulation wavelength decreases. It should be noted that κ_{eff} defined in Eq. (18) is practically amplitude independent (within ±0.3%). This can be easily seen if $(\Delta U_e/V)_{\text{app}}$ is employed in place of $\Delta U_e/V$ in Eq. (18). Since the gradient energy is related to the interfacial energy,[1] the above feature directly corresponds to the decrease of the effective surface energy of a spherical void when its radius decreases,[11,12] as previously mentioned. Thus, the physical background of Figs. 1 and 3 is common. Finally it should be emphasized that, when nucleation phenomena in metallic systems are treated,
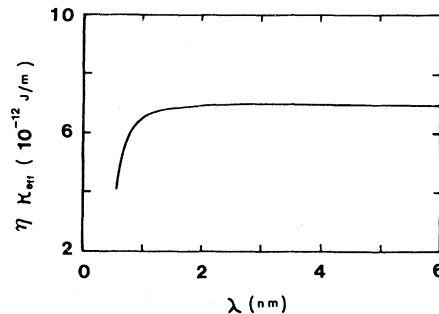

FIG. 3. Wavelength λ dependence of effective-gradient-energy coefficient κ_{eff} [defined in Eq. (18)], in Cs—50 at. % Rb. Here, $\eta = [n_0/(n_A - n_B)]^2$.

the decrease of the effective gradient-energy coefficient or the interfacial energy, as the dimension of nuclei decreases, must be properly taken into account.

IV. CONCLUSION

With the use of the Hohenberg-Kohn formula for the ground-state energy of a nonuniform electron-gas system in a jellium model, electronic excess energy or the difference in electronic energy between the homogeneous solution and one with a sinusoidally modulated composition was derived. By means of a fully numerical calculations, the validity of an approximate expression which had previously been utilized was ensured. The electronic excess energy increased as the modulation wavelength decreases. An effective gradient-energy coefficient was shown to decrease as the wavelength decreased. This was caused by the fact that electrons rather stayed flattened compared with the distribution of positive charges. This may be significant when small nuclei in metallic systems are theoretically treated.

ACKNOWLEDGMENT

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