PHYSICAL REVIEW B VOLUME 8, NUMBER 4 15 AUGUST 1973

Simple Mean-Field Approach to Phase Separation in Liquid-Metal Alloys*

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(Received 14 December 1972)

A mean-field theory of phase separation in liquid-metal alloys is described. The method satisfactorily accounts for the variation of critical concentration in alloys of simple metals, and also gives critical temperatures in reasonably good agreement with experiment. It predicts that under pressure the critical temperature should rise proportionally to the ionic number density. The theory leads to typical mean-field divergences in the x-ray scattering intensity, specific heat, and temperature derivative of the resistivity. The relation between the instability that causes such divergences and the "freezing instability" described by Schneider *et al.* is discussed.

I. INTRODUCTION AND CONCLUSIONS

The properties of binary liquid-metal alloys with a miscibility gap have recently been the subject of much experimental interest.[1-6] The main concern of such studies has been fluctuation effects above the critical point for phase separation. Anomalies have been reported in the x-ray[1] and neutron[2] scattering intensities, specific heat,[6] and electrical resistivity[3-5] near the critical point.

By contrast, theoretical studies[7,8] have been confined to attempted calculations of the phase-separation curve itself, and the models used thus far cannot account for fluctuation effects. The model of Ref. 7 (hereafter referred to as I), for example, leads to a calculated phase-separation curve in rather good agreement with experiment. The curve is determined there by means of a common-tangent construction applied to the free-energy isotherms (see Fig. 1). The free energy is obtained variationally, using hard-sphere structure factors to evaluate the ion-ion interaction energy and the entropy. This approach can never lead to divergent concentration fluctuations because, as is well known, hard-sphere structure factors, at least in the Percus-Yevick[9] approximation, exhibit no divergences at any concentration and temperature.[10] Indeed, phase separation occurs at all, in the model of I, only because the free energy, unlike the structure factors, does differ from that of a simple mixture of hard spheres.

It is the purpose of this paper to present a simple mean-field model for phase separation in liquid-metal alloys. The critical point will be determined within this model as the maximum temperature T_c, and corresponding concentration x_c, at which concentration fluctuations diverge. This choice, unlike the approach of I, automatically ensures that a number of experimental quantities directly dependent on such fluctuations will also diverge at T_c. Thus the present study represents the first microscopic theory of phase separation in liquid-metal alloys that is also capable of describing, albeit very crudely, fluctuations above the critical point.

To calculate the structure factors, it will be assumed that, under the action of an infinitesimal external field, each ion responds like a *free particle* to the *mean field* acting on it. The mean field consists of the external field plus the self-consistently determined field due to the induced charge densities of the other ions. The response functions thus obtained are related to the structure factors by the fluctuation-dissipation theorem.

It is rather surprising that this crude model is capable of producing a critical point for phase separation, as well as several fluctuation effects above T_c. Yet the critical temperatures, and, especially, the critical concentrations calculated by this approach for a number of alloys, are in

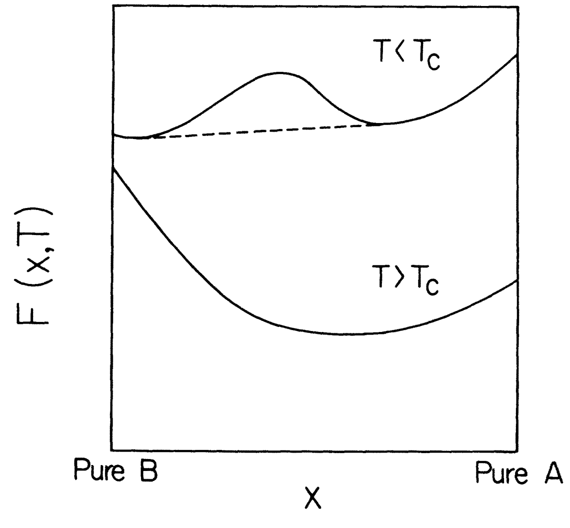

FIG. 1. Schematic of behavior of Helmholtz-free-energy isotherm $F(x, T)$ in an alloy with a miscibility gap. For $T > T_c$, $\partial^2F/\partial x^2 > 0$ at all concentrations. For $T < T_c$, the limits of solubility are given by the intersection of the isotherm with a common tangent (dashed line). This is the method used in Ref. 7 to find the phase boundary in $\mathrm{Li}_x\mathrm{Na}_{1-x}$.

good agreement with experiment, even though obtained without benefit of any free parameters. Indeed, the theory appears to account completely for the systematic variation of x_c from one alloy system to another. It is found that x_c is determined primarily by valence differences between the alloy constituents, or, in isovalent alloys, by differences in atomic volume and effective ionic radius. The critical exponents yielded by the theory are, of course, mean field. Thus, for example, the x-ray scattering intensity $I(\vec{q}, T)$ at scattering vector $\vec{q}$ varies as $[a(T-T_c)+bq^2]^{-1}$, the specific heat $C_{V,x}$ at constant volume and concentration diverges as $(T-T_c)^{-1/2}$, and the first temperature derivative of the resistivity diverges as $\ln(T-T_c)$. Although a more elaborate theory, such as an approach using as a zeroth approximation a hard-sphere liquid rather than a gas of free particles, might lead to different, and more accurate, *coefficients* for these divergences, it would invariably give the same *exponents*.

As a by-product of this investigation, it is possible to suggest a connection between the instability that leads to phase separation and the "freezing instability" discussed by Schneider *et al.*[11] The critical point for phase separation is determined in the present approach by the condition that a certain function $\hat{D}(q, T, x)=0$ at $q=0$ and $x=x_c$. For any q and x, $\hat{D}(q, T, x)$ happens to be quadratic in T. The solution corresponding to phase separation is readily isolated. The other solution appears to be related to the freezing instability. In the present crude model, the freezing-instability temperatures are all negative. For a more elaborate model, they are probably positive at certain values of q, thus leaving open the possibility that the mixture might be unstable below some temperature against the formation of a finite-wavelength *density* fluctuation. This tendency may possibly be competing with the instability against an infinite-wavelength *concentration* fluctuation which leads to phase separation.

The results of this work call attention to a paradox implicit in the method. Using free-energy isotherms obtained from the present mean-field theory, we can find the phase-separation line by the common-tangent construction illustrated in Fig. 1. The critical point so determined does not coincide with that found by the criterion of divergent concentration fluctuations. In an exact theory, of course, the two must be identical. The discrepancy is inevitable in approximate approaches. In the present approach, the free energy is highly inaccurate, being based on structure factors that do not exhibit any peaks. Thus it is far preferable to find the critical point in this case from the fluctuation condition, rather than from the common-tangent construction.

We turn now to the body of the paper. Section II describes the mean-field method of calculating the structure factors, and Sec. III applies the method to liquid-metal alloys with a miscibility gap.

II. MEAN-FIELD THEORY

Consider a liquid-metal alloy A_xB_{1-x}. If the alloy has volume Ω, the three structure factors $S_{AA}(q)$, $S_{AB}(q)$, and $S_{BB}(q)$ are defined by

$$S_{ij}(q) = \left((N_iN_j)^{-1/2}\left\langle \sum_{\vec{R}_i,\vec{R}_j} e^{i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)}\right\rangle - (N_iN_j)^{1/2}\delta_{q0}\right)\Omega, \quad (1)$$

where N_i is the number density of the ith component, $\vec{R}_i$ is a position vector of an ion of type i, and the brackets denote an ensemble average.

It is convenient to find an expression for the structure factors in the long-wavelength limit via the corresponding susceptibilities $\chi_{ij}(\vec{q}, \omega)$. These are most easily defined in terms of an infinitesimal external perturbation

$$H' = \Omega^{-1}[n_A(-\vec{q})\delta V_A^{\mathrm{ext}}(\vec{q}\omega) + n_B(-\vec{q})\delta V_B^{\mathrm{ext}}(\vec{q}\omega)]e^{-i\omega t} , \quad (2)$$

where

$$n_i(\vec{q}) = \int e^{i\vec{q}\cdot\vec{r}} n_i(\vec{r})\,d\vec{r}$$

is the (number) density of the ith ionic species, and $\delta V_i^{\mathrm{ext}}(\vec{q}\omega)e^{-i\omega t}$ is the Fourier component of the external potential acting on the ith species at time t. Since H' is infinitesimal, it induces ionic densities $\delta n_i(\vec{q}t)=\delta n_i(\vec{q}\omega)e^{-i\omega t}$ linear in the δV_i's. The susceptibilities $\chi_{ij}(q\omega)$ are then defined by the relations

$$\delta n_i(\vec{q}\omega) = \sum_j \chi_{ij}(\vec{q}\omega)\delta V_j^{\mathrm{ext}}(q\omega) , \quad (3)$$

where the indices i and j take on the values A and B.

The mean-field approximation consists of the assumption that each ion responds like a free particle to the mean field acting on it. Thus

$$\delta n_i(\vec{q}\omega) \sim \chi_i^0(\vec{q}\omega)\delta V_i^{\mathrm{eff}}(q\omega) , \quad (4)$$

where $\chi_i^0(\vec{q}\omega)$ is the free-particle susceptibility of the ith species, and $\delta V_i^{\mathrm{eff}}(\vec{q}\omega)$ is the mean field acting on the ith species. If the interaction between the ions is adequately described by local pair potentials $W_{ij}(\vec{r})$, then

$$\delta V_i^{\mathrm{eff}}(\vec{q}\omega)e^{-i\omega t} = \delta V_i^{\mathrm{ext}}(\vec{q}\omega)e^{-i\omega t} + \sum_j\left(\int e^{i\vec{q}\cdot\vec{r}}\,d\vec{r}\int W_{ij}(\vec{r}-\vec{r}')\delta n_j(\vec{r}')\,d\vec{r}'\right)e^{-i\omega t}$$

$$= \left(\delta V_i^{\text{ext}}(\vec{q}\omega) + \sum_j W_{ij}(q) \delta n_j(\vec{q}\omega) \right) e^{-i\omega t} , \tag{5}$$

where

$$W_{ij}(q) = \int e^{i\vec{q}\cdot\vec{r}} W_{ij}(r)\, d\vec{r}.$$

Substituting (5) into (4), solving for δn_A and δn_B, and comparing coefficients with the definitions (3), we obtain

$$\begin{aligned} \chi_{AA} &= (1 - \chi_B^0 W_{BB}) \chi_A^0 / D , \\ \chi_{BB} &= (1 - \chi_A^0 W_{AA}) \chi_B^0 / D , \\ \chi_{AB} &= \chi_{BA} = W_{AB} \chi_A^0 \chi_B^0 / D , \\ D &= (1 - \chi_A^0 W_{AA})(1 - \chi_B^0 W_{BB}) - \chi_A^0 \chi_B^0 W_{AB}^2 , \end{aligned} \tag{6}$$

where we have suppressed indices $\vec{q}$ and ω.

The structure factors $S_{ij}(q)$ are related to the corresponding susceptibilities by the fluctuation-dissipation theorem:

$$S_{ij}(q) = -(N_i N_j)^{-1/2} \frac{\hbar}{\pi} \int_0^\infty \coth \tfrac{1}{2} \beta \hbar \omega \operatorname{Im} \chi_{ij}(q\omega)\, d\omega , \tag{7}$$

where $\beta = (k_B T)^{-1}$. In the classical limit ($\hbar \to 0$), Eq. (7) reduces by application of the Kramers-Kronig relations to the well-known expression[12]

$$S_{ij}(q) = -(N_i N_j)^{-1/2} k_B T \chi_{ij}(q0) . \tag{8}$$

Substituting (6) into (8), and using $\chi_i^0(q, 0) = -\beta N_i$, we find

$$\begin{aligned} S_{AA}(q) &= [1 + \beta y \hat{W}_{BB}(q)] / \hat{D}(q, \beta, x) , \\ S_{BB}(q) &= [1 + \beta x \hat{W}_{AA}(q)] / \hat{D}(q, \beta, x) , \\ S_{AB}(q) &= S_{BA}(q) = -\beta [x(1 - x)]^{1/2} \hat{W}_{AB}^2(q) / \hat{D}(q, \beta, x) , \end{aligned} \tag{9}$$

with

$$\hat{D}(q, \beta, x) = [1 + \beta x \hat{W}_{AA}(q)][1 + \beta y \hat{W}_{BB}(q)] - \beta^2 x y \hat{W}_{AB}^2(q) . \tag{10}$$

Here $y = 1 - x$, and $\hat{W}_{ij}(q) = N W_{ij}(q)$ has dimensions of energy, $N = N_A + N_B$ being the total number of ions per unit volume.

Equations (9) and (10) are merely the two-component generalization of the mean-field structure factors $S(q) = [1 + \beta N \hat{W}(q)]^{-1}$ for a single-component fluid. As such, they share the defects of the latter approximation, namely, (a) they fail to predict the first peak in the structure factors of liquid metals; (b) they are inapplicable to systems described by Lennard-Jones pair potentials, whose Fourier transforms do not exist. Both shortcomings arise from a failure to take proper account of the short-range correlations in the liquid. Equations (9) and (10) involve the Fourier transforms of the pair potential $W_{ij}(r)$ over the *entire* range of ionic separation. Yet the quantitative behavior of the pair potential can have no physical significance for separations less than some effective hard-core diameter d_{hc}, within which the potential is never actually sampled. In a more accurate approach, one might expect that $W_{ij}(q)$ would be replaced by a quantity like

$$W_{ij}(q) = \int e^{i\vec{q}\cdot\vec{r}} g_{ij}^{\text{hc}}(r) W_{ij}(r)\, d\vec{r} ,$$

where $g_{ij}^{\text{hc}}(r)$ is a hard-core pair correlation function. Such an approach will give well-behaved functions $\hat{W}_{ij}(q)$ even for a Lennard-Jones potential, and in addition correctly predicts the first peak in the structure factor.[11]

In a system undergoing phase separation, the phase transition is accompanied by correlations extending over an anomalously long range, and not necessarily by anomalous behavior in the short-range correlations responsible for the first peak in the structure factor. It is therefore plausible that the present mean-field approach, though it fails to account for the first peak, will give a reasonable qualitative description of some aspects of the phase transition.

Before turning to the subject of phase separation, we note that the Helmholtz free energy can be explicitly evaluated within the mean-field approximation, via the well-known coupling-constant integral for the free energy[13]:

$$F - F_0 = \int_0^1 \langle V \rangle_\lambda\, d\lambda . \tag{11}$$

Here F is the free energy per ion, F_0 the free energy of a system of noninteracting ions (i.e., all terms in the free energy which do not depend on ionic configuration), and $\langle V \rangle_\lambda$ is the expectation value of the ion-ion interaction, calculated using structure factors $S_{ij}^\lambda(q)$ appropriate to a system with pair potentials $\lambda W_{ij}(r)$. Thus

$$\begin{aligned} \langle V \rangle_\lambda = \tfrac{1}{2} N \sum_{\vec{q} \neq 0} \{ & x W_{AA}(q) [S_{AA}^\lambda(q) - 1] \\ & + 2[x(1 - x)]^{1/2} W_{AB}(q) S_{AB}^\lambda(q) \\ & + (1 - x) W_{BB}(q) [S_{BB}^\lambda(q) - 1] \} , \end{aligned} \tag{12}$$

where the structure factors $S_{ij}^\lambda(q)$ are given by Eqs. (9) and (10), with all factors $\hat{W}_{ij}(q)$ replaced by $\lambda \hat{W}_{ij}(q)$. The term $\vec{q} = 0$ is included in F_0. Substituting Eqs. (9), (10), and (12) into (11), and carrying out the coupling-constant integration, we find

$$F - F_0 = \frac{1}{2} \sum_{q \neq 0} [k_B T \ln \hat{D}(q, \beta, x) - x \hat{W}_{AA}(q) - (1 - x) \hat{W}_{BB}(q)] . \tag{13}$$

Note that this expression is the generalization of the one-component mean-field result

$$F - F_0 = \frac{1}{2} \sum_{\vec{q} \neq 0} \{k_B T \ln[1 + \beta N W(q)] - W(q)\}, \qquad (14)$$

which is obtained, for example, in the random-phase-approximation (RPA) theory of the Ising and Heisenberg ferromagnets.[14]

III. PHASE SEPARATION

In a liquid-metal alloy of critical concentration, as in other binary mixtures, the onset of phase separation is signaled by concentration fluctuations that diverge as T approaches the critical temperature T_c from above. This effect is mirrored in the three partial structure factors S_{AA}, S_{AB}, and S_{BB}, which satisfy

$$S_{ij}(0) \to \infty \text{ as } T \to T_c . \qquad (15)$$

Equation (15) actually defines a *line* of critical temperatures $T_s(x)$, one for each alloy concentration. Only the highest critical temperature $T_c = T_s(x_c)$, corresponding to the critical concentration x_c, is attainable physically. At other concentrations, the critical line is masked by the phase boundary. The latter is determined by a common-tangent construction applied to the free-energy isotherms (see Fig. 1), and lies at temperatures higher than the critical line, except at $x = x_c$.

In the present mean-field approach, condition (15) is seen from Eqs. (9) and (10) to be equivalent to the requirement that at $q = 0$

$$\hat{D}(q, \beta_c, x) = 0 , \qquad (16)$$

where $\beta_c = 1/k_B T_c$. Since $D(q, \beta, x)$ is a quadratic in β (or T), Eq. (16) has two solutions for each concentration and wave vector, $T_s(q, x)$ and $T_f(q, x)$. Clearly, the solution $T_s(q, x)$ corresponding to phase separation must tend to zero at $q = 0$ in the low-concentration limit $x \to 0$ or $x \to 1$, and in the "virtual monocomponent" limit $W_{AA}(q) = W_{AB}(q) = W_{BB}(q)$, since the mixture in these limits is stable against separation at all temperatures. $T_f(q, x)$, the other solution, may tentatively be identified as a prototype of the "freezing-instability line" described by Schneider *et al.*[11] We may isolate this latter solution by examining $\hat{D}(q, \beta, x)$ in either the low-concentration or the virtual monocomponent limit. Then Eq. (16) becomes

$$\hat{D}(q, \beta, x) \to 1 + \beta \hat{W}(q) = 0$$
$$\text{for } x \to 0 \text{ or } W_{AA} = W_{AB} = W_{BB} = W . \qquad (17)$$

For a liquid metal, $\hat{W}(q)$ is positive for all q, and the solutions $T_f(q)$ to Eq. (17) are negative for all q. $T_f(q, x)$ proves to be negative in the alloy also. It was shown in Ref. 11 that for a more refined model $T_f(q)$ is positive for q's in the vicinity of the first reciprocal-lattice vector in the corresponding crystal, and thus may possibly be approached by supercooling the liquid phase.

Equation (16) is readily solved for $T_s(q, x)$ if a realistic model can be found for the pair potentials. For an alloy of nearly-free-electron metals, as is well known, such potentials are available analytically in q space in terms of the electron-ion pseudopotentials[15]:

$$W_{ij}(q) = \frac{4\pi Z_i Z_j e^2}{q^2} + \frac{q^2}{4\pi e^2} V_i(q) V_j(q) \left(\frac{1}{\epsilon(q)} - 1 \right) . \qquad (18)$$

Here $Z_i e$ is the charge of the ith species of ion, $V_i(q)$ is the unscreened pseudopotential of the ith species of ion (assumed local and energy independent) and $\epsilon(q)$ is the dielectric function for the free interacting electron gas. The first term in (18) represents the direct (Coulomb) interaction between the ions, while the second corresponds to an indirect interaction through polarization of the electron gas. If the pseudopotential is not small, it will be necessary to take into account terms of third or higher order in the pseudopotentials. These are thought to correspond to three-body or multibody interactions between the ions, and will not be considered here.

Since the solutions $T_s(q, x)$ are of particular interest in the region $q \sim 0$, it is imperative that the pair potentials $W_{ij}(q)$ be accurate in this long-wavelength limit. In the present calculations, the pseudopotential has been chosen to be of the empty-core variety,[16]

$$V_i(q) = -(4\pi Z_i e^2 / q^2) \cos q r_c^i, \qquad (19)$$

with the single parameter r_c^i fitted to the zero-pressure zero-temperature density of a pure *solid* of species i, a quantity very sensitive to the long-wavelength limit of the pseudopotential. The fitting procedure is described in the Appendix. The resulting r_c's are listed in Table I, where they are compared with the same parameters as fitted to the zeros of Heine-Abarenkov[17] pseudopotentials. $\epsilon(q)$ has been taken to be of the modified Hubbard form[18]:

$$\begin{aligned} \epsilon(y) &= 1 + (0.166 r_s / y^2) \hat{f}(y) , \\ \hat{f}(y) &= \frac{f(y)}{1 - 0.166 r_s f(y)/(2y^2 + g)} , \\ f(y) &= \frac{1}{2} + \frac{1}{4y}(1 - y^2) \ln \left| \frac{1+y}{1-y} \right| , \qquad (20) \\ g &= (1 + 0.026 r_s)^{-1} , \\ y &= k/2k_F . \end{aligned}$$

Here, k_F is the Fermi wave vector, and $\frac{4}{3}\pi r_s^3 = \Omega_0 / Z$ is the volume per valence electron. So chosen, $\epsilon(y)$ satisfies[19] the compressibility sum rule $\lim[y^2 \epsilon(y)] = K_0/K$ as $y \to 0$, where K_0 and K are the compressibilities of the noninteracting and interacting electron gas, the latter being calculated

TABLE I. Core radii r_c as used to calculate the critical points. The quantities in brackets are the core radii determined by fitting the first zero of the Heine-Abarenkov pseudopotential to the model pseudopotential (19).

Element	r_c (a.u.)
Li	1.332 [1.73]
Na	1.728 [1.81]
Zn	1.245 [1.11]
Hg	1.363 [1.24]
Ga	1.199 [1.10]
Bi	1.104 [1.12]

from the Nozieres-Pines[20] approximation for the correlation energy of the electron gas.

Table II lists the critical temperatures T_c and critical concentrations x_c, as calculated from Eq. (16), for four liquid alloys. Atomic volumes have been assumed to vary linearly with x. Experimental quantities are in parentheses. Agreement with experiment is remarkably good, especially considering that the calculations involve no free parameters. The discrepancies in the critical temperatures of $\mathrm{Ga}_x\mathrm{Bi}_{1-x}$ and $\mathrm{Zn}_x\mathrm{Bi}_{1-x}$ may certainly be accounted for in part by the peculiarities of Bi, which is nearly a semimetal in the solid phase and therefore may not adequately be described by the present second-order-perturbation scheme in the liquid phase. More significantly, the calculated critical temperatures are extremely sensitive to small changes in the pseudopotential, a 1% change in r_c^{Bi}, for example, leading to a change of about one-half in the critical temperature of $\mathrm{Ga}_x\mathrm{Bi}_{1-x}$. The critical concentrations, by contrast, are insensitive to such discrepancies.

These results can be better understood in the limit

$$x(1-x)\,|\hat{W}_{AB}^2(0)-\hat{W}_{AA}(0)\hat{W}_{BB}(0)| \ll |x\hat{W}_{AA}(0)+(1-x)\hat{W}_{BB}(0)|^2\,, \tag{21}$$

which holds well for the present applications. Then, from (10) and (16), the critical line $T_s(x)$ is given approximately by the expression

$$k_B T_s(x) \approx x(1-x)N\,\frac{W_{AB}^2(0)-W_{AA}(0)W_{BB}(0)}{xW_{AA}(0)+(1-x)W_{BB}(0)}\,. \tag{22}$$

The critical concentration x_c corresponds to the maximum temperature $T_c = T_s(x_c)$ on the critical line. The concentration dependence of $T_s(x)$ is contained in the prefactor $x(1-x)N$ and in the denominator, the "average pair potential":

$$W_{\mathrm{av}}(0) = xW_{AA}(0)+(1-x)W_{BB}(0)\ .$$

From (18)–(20), it is found that

$$W_{ii}(0) = 4\pi Z_i^2 e^2\left((r_c^i)^2 + \frac{1}{4k_F^2}\,\frac{K}{K_0}\right). \tag{23}$$

As a rule, the first term in the large parentheses of (23) proves to be considerably larger than the second. From (23), $W_{\mathrm{av}}(0)$ is evidently insensitive to small changes in r_c^A and r_c^B. On the other hand, T_c, which is proportional to $W_{AB}^2(0)-W_{AA}(0)W_{BB}(0)$, varies approximately as $[(r_c^A)^2-(r_c^B)^2]^2$ and thus depends critically on such changes.

In the absence of concentration dependence in N and $W_{\mathrm{av}}(0)$, expression (22) leads to a symmetric critical line $T_s(x) \propto x(1-x)$, with a maximum at $x = 0.5 = x_c$. If N and $W_{\mathrm{av}}(0)$ depend significantly on concentration, the critical line will tend to be skewed towards concentrations where N is larger or where $W_{\mathrm{av}}(0)$ is smaller. If the alloy constituents have different valences, the curve, from Eq. (23), tends to be skewed towards the side of lower electron-to-atom ratio. In $\mathrm{Ga}_x\mathrm{Bi}_{1-x}$ and $\mathrm{Zn}_x\mathrm{Bi}_{1-x}$, this is very much the dominant effect in controlling the skewness. In an isovalent alloy, the curve is skewed towards larger N or smaller r_c. In $\mathrm{Li}_x\mathrm{Na}_{1-x}$, these effects reinforce one another and the calculated critical concentration is 62-at.% Li (versus an experimental value of 65 at.%).

Equation (22) also predicts a simple behavior of T_c and x_c under applied pressure, namely, if the pair potentials $W_{ij}(0)$ do not depend on density,

$$T_c(N) \propto N, \quad x_c(N) \sim \text{const.} \tag{24}$$

Such behavior does not depend on approximation (21), but follows from the general solutions to Eq. (16). In fact, the pair potentials $W_{ij}(q)$ are N dependent through the N dependence of $\epsilon(q)$, but at small q this dependence is much weaker than lin-

TABLE II. Calculated critical concentrations x_c and temperatures T_c for four liquid alloys. Experimental values are in brackets. Discrepancies in the critical temperatures of the Bi-based alloys result principally from the extreme sensitivity of T_c to very small changes in the parameters characterizing the pseudopotentials (see text).

Alloy	x_c	T_c
$\mathrm{Li}_x\mathrm{Na}_{1-x}$	0.62 [0.65[a]]	650 [580[a]]
$\mathrm{Ga}_x\mathrm{Hg}_{1-x}$	0.44 [0.50[b]]	406 [475[b]]
$\mathrm{Ga}_x\mathrm{Bi}_{1-x}$	0.62 [0.70[c]]	157 [535[c]]
$\mathrm{Zn}_x\mathrm{Bi}_{1-x}$	0.75 [0.83[c]]	438 [878[c]]

[a] Reference 5. [b] Reference 6. [c] Quoted in Ref. 2.

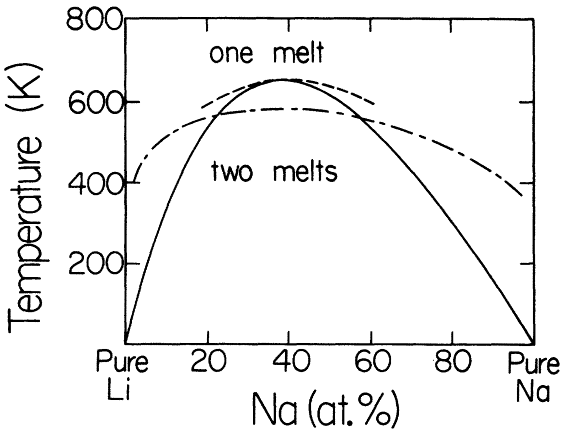

FIG. 2. Solid line: critical line for phase separation in liquid Li_xNa_{1-x}, as calculated from mean-field theory. Dashed line: schematic of phase boundary of a system having such a critical line. Dot-dashed line: experimental phase boundary, as listed in Ref. 7.

ear, and so (24) should remain approximately valid.

Figure 2 displays the critical line $T_s(x)$ for Li_xNa_{1-x}, as calculated from Eq. (16). For comparison, the experimental phase-separation curve has also been plotted, as has a schematic of the phase-separation curve corresponding to a system having the calculated critical line. The construction of Fig. 1, applied to the free energy (13), would actually lead to a phase boundary with a different critical point (see Sec. I). Note that near the critical concentration, the mean-field critical line varies like $T_s(x_c) - T_s(x) = \text{const.} \times |x - x_c|^{1/\beta}$, with $\beta = 0.5$. Experimentally,[5] $\beta = 0.30$–0.35; the discrepancy is characteristic of mean-field theories.

The critical temperatures $T_s(q, x)$ and $T_f(q, x)$ for Li_xNa_{1-x}, as obtained from Eq. (16), are plotted versus q in Fig. 3. As expected, the maximum T_s occurs at $q=0$. Thus it is the long-wavelength concentration fluctuations which diverge at T_c, as indeed must be the case if T_c is to represent the critical temperature for the usual kind of phase separation. If the maximum occurred at finite q, the critical point would evidently correspond to an instability with respect to some kind of short-wavelength concentration fluctuation. Such an instability has apparently never been observed. Figure 2 also shows that within the mean-field model the hypothetical "freezing-instability line" $T_f(q, x_c)$ is always negative. The dashed curve is a schematic illustration of the same curve as it might appear in a more elaborate theory, such as a two-component generalization of the approach of Ref. 11, the maximum (at a positive temperature) possibly attainable by supercooling.

We turn now to the various static critical effects associated with the divergent concentration fluctuations above T_c. It may be shown from Eqs. (16) and (10) that near the critical point and at small q

$$\hat{D}(q, \beta, x) = a(T - T_c) + b(x - x_c)^2 + cq^2 , \tag{25}$$

where a, b, and c are positive constants. Equation (25) has several direct consequences. For example, the small-angle x-ray scattering intensity $I(q)$ from the alloys is given by

$$I(q) = xf_A^2(q)S_{AA}(q) + 2[x(1-x)]^{1/2} f_A(q) f_B(q) S_{AB}(q) + (1-x) f_B^2(q) S_{BB}(q) \propto [a(T - T_c) + b(x - x_c)^2 + cq^2]^{-1} , \tag{26}$$

where $f_A(q)$ and $f_B(q)$ are the appropriate atomic form factors. At $q=0$ and $x = x_c$, $I \propto (T - T_c)^{-1}$. Such divergences have been seen in liquid Li_xNa_{1-x}.[1] The exponent has not been tested experimentally in liquid metals, though the mean-field result is certainly not correct. Also from Eqs. (25) and (13), the divergent part of the specific heat at constant volume and concentration, $\Delta c_{V,x}$, is

$$\Delta c_{V,x} = -T \frac{\partial^2}{\partial T^2}(F - F_0) \propto [a(T - T_c) + b(x - x_c)^2]^{-0.5} . \tag{27}$$

Experimentally,[6] $\Delta c_{P, x=x_c} \propto (T - T_c)^{-0.33}$. $\Delta c_{V, x=x_c}$ should exhibit the same behavior. Thus, the exponent in (27) is in typical mean-field disagreement with experiment. Finally, the compressibility at constant temperature and concentration,

$$\chi_{T,x} = (Nk_B T)^{-1}$$

$$\times \frac{S_{AA}(0)S_{BB}(0) - S_{AB}^2(0)}{xS_{BB}(0) + (1-x)S_{AA}(0) - 2[x(1-x)]^{1/2} S_{AB}(0)} , \tag{28}$$

is found from Eqs. (25) and (9) to be finite at the critical point, because divergences in the numerator and denominator cancel. It is not surprising that $\chi_{T,x}$ remains finite, because it corresponds to long-wavelength *density* fluctuations, while it is long-wavelength *concentration* fluctuations that are divergent at T_c.

A quantity of considerable interest is the temperature derivative of the resistivity $(\partial\rho/\partial T)_{V,x}$ near the critical point. For a liquid-metal alloy, the resistivity is given to second order in the pseudopotentials[19] by

$$\rho = C \int_0^{2k_F} dq\, q^3 \{ x\tilde{V}_A^2(q) S_{AA}(q)$$

$$+ 2[x(1-x)]^{1/2} \tilde{V}_A(q) \tilde{V}_B(q) S_{AB}(q)$$

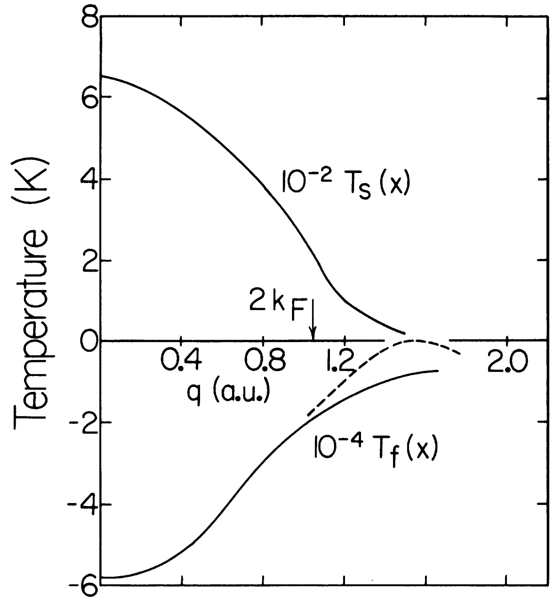

FIG. 3. $T_s(q)$ and $T_f(q)$ for liquid $Li_{0.62}Na_{0.38}$. The dashed curve is a schematic of $T_f(q)$ as it might be in a more elaborate theory, such as that of Ref. 11. Note differences of scale between the curves.

$$+(1-x)\tilde{V}_B^2(q)S_{BB}(q)\}\ , \qquad (29)$$

where $\tilde{V}_i(q)=V_i(q)/\epsilon(q)$ is the (screened) pseudopotential form factor for an ion of species i, and C is a constant depending weakly on the concentration. Substituting (9), (10), and (25) into (29), we find that the divergent part of the temperature derivative, which we will write $\Delta\rho'_{V,x}(x, T) = \partial\Delta\rho(x, T)/\partial T\,|_{V,x}$, satisfies

$$\Delta\rho'_{V,x}(x, T)\propto \ln[a(T-T_c)+b(x-x_c)^2] \quad (T>T_c)\ , \qquad (30)$$

so that

$$\Delta\rho'_{V,x}(x_c, T)\propto \ln(T-T_c) \quad (T>T_c)\ ,$$
$$\Delta\rho'_{V,x}(x, T_c)\propto \ln|x-x_c|\ . \qquad (31)$$

The experimental divergences are stronger than logarithmic in Li_xNa_{1-x}.[5] In Ga_xHg_{1-x} divergences have been sought but not found.[5] Fisher and Langer[21] predict on general grounds a divergence proportional to the divergences in the specific heat. For liquid-metal alloys, no microscopic model exists which leads to this prediction. A logarithmic divergence is probably built into any mean-field theory, even one more refined than the present model. These experimental anomalies thus remain basically unexplained.

ACKNOWLEDGMENTS

I have profited from valuable conversations with Professor N. W. Ashcroft and with R. Henderson. Parts of this work were accomplished while I was a visitor at the Aspen Physics Center and at Cornell University, for whose hospitality I am most grateful.

APPENDIX: PROCEDURE FOR FITTING r_c

The single parameter r_c specifying the electron-ion psuedopotential (19) for a given species of ion may be determined by requiring that the zero-pressure zero-temperature density of the solid phase be correctly reproduced. Thus r_c is chosen so that at $\Omega=\Omega_0$

$$\left(\frac{\partial E}{\partial\Omega}\right)_{T=0}=0\ , \qquad (A1)$$

where E is the energy per ion in the solid phase at 0 K, Ω is the volume per ion, and Ω_0 the correct zero-pressure volume per ion.

To second order in the pseudopotential,

$$E\sim E_{eg}+E_M+E_{BS}+E_0 \qquad (A2)$$

where E_{eg} is the electron-gas energy (including kinetic, exchange, and correlation energy), E_M is the Madelung energy, E_{BS} is the electron-ion energy, and E_0 is the "Hartree" energy. The latter is the sum of the $q=0$ Fourier components of the (bare) ion-ion, electron-electron, and electron-ion interactions. For pseudopotential (18),

$$E_0(\Omega)=\lim_{q\to 0}\left(\frac{4\pi e^2}{q^2}+V(q)\right)=\frac{2\pi e^2 r_c^2}{\Omega}\ . \qquad (A3)$$

Convenient expressions for the other three terms in (A2) have been given, for example, by Ashcroft and Langreth.[22] E_{BS}, of course, depends on the pseudopotential also, but only for $q\sim 2k_F$, k_F being the Fermi wave vector. Since the calculations of Sec. III depend on $V(q)$ only in the long-wavelength limit, it is sufficient for their purposes to determine E_{BS} using a standard pseudopotential. In the present paper, E_{BS} has been calculated from the empty-core pseudopotential (19), with r_c fitted to the first zero of the Heine-Abarenkov form factors.[17] To simplify the computation, the fitting has been done in all cases for an assumed fcc crystal structure. Since the binding energies do not vary much with crystal structure, this approximation should lead to little error. The prescription is then sufficient to determine $E(\Omega)$. Equation (A2) is then readily solved for r_c, with results as tabulated in Sec. III.

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*Supported in part by the National Science Foundation under Grant No. GH-33746.

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PHYSICAL REVIEW B VOLUME 8, NUMBER 4 15 AUGUST 1973

Anharmonic Contributions to Elastic and Inelastic Scattering of X Rays at Bragg Reflections in Aluminum

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(Received 4 December 1972)

The scattering intensities of the 14.4-KeV γ rays from Co^{57} were measured at the $\{333\}$ and $\{444\}$ reflections of Al crystals in the temperature range 295-800 °K. The elastic and inelastic components of the scattered intensities were separated by means of the Mössbauer effect. The temperature dependences of the integrated intensities of the elastic peaks give evidence of non-Gaussian anharmonic contributions to the Debye–Waller factors. Comparison is also made between experimental and calculated temperature dependences of the inelastic intensities. Some of the discrepancies found at the $\{444\}$ reflection are explained by admitting a non-neglectable contribution of non-Gaussian terms in the correlation part of the formula for the intensity of the thermal diffuse scattering.

I. INTRODUCTION

As is known, the thermal motion of the atoms in a crystal lattice causes a weakening of the Bragg diffraction lines and an increase in the total amount of the thermal diffuse scattering (TDS). Thus, in principle, x-ray-diffraction experiments can give information about the dynamics of the lattice. For example, the mean-square vibration amplitude of the atoms can be obtained from the temperature dependence of the integrated intensities of Bragg peaks, whereas by measuring the TDS intensity at different sites in the Brillouin zone one can obtain the dispersion curves of the lattice phonons.[1] The greatest part of experimental research in this field is mainly related to the atomic motion as described in the harmonic approximation.

The suggestion that diffraction experiments would also be useful to give evidence of anharmonic effects was first given by Waller.[2] Since then a lot of theoretical and experimental investigations have been performed, especially regarding the anharmonic contributions to the Debye-Waller factor. However, in order to separate anharmonic effects it is often necessary to make experiments at high-order reflections and at elevated temperatures. In these experimental conditions the intensity scattered at a reciprocal-lattice node is quite appreciably made up of those x-ray photons which suffer inelastic scattering by the thermal vibrations of the lattice. Both elastic and inelastic scatterings are affected by anharmonic interactions. However, it is necessary to separate them in order to obtain substantiated information on the amount of anharmonic contributions.

The only way to accurately separate the TDS from the crystalline reflections is to use the high-energy resolution of the Mössbauer effect. This