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S. Dorfman, D. Fuks, A. Gordon. Landau Theory in Kinetics of the CuAu First-Order Phase Transition. Journal de Physique IV Proceedings, 1996, 06 (C1), pp.C1-35-C1-43. 10.1051/jp4:1996104 . jpa-00254135

HAL Id: jpa-00254135

<https://hal.science/jpa-00254135>

Submitted on 1 Jan 1996

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Landau Theory in Kinetics of the CuAu First-Order Phase Transition

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Abstract. The study of kinetics of the order-disorder phase transition in *CuAu* is performed in the framework of the time-dependent Ginzburg-Landau theory. The analytical solution for the motion parameters of the interphase boundary is applied to the calculations of width and velocity at different overheating and overcooling temperatures. We propose a way of verification of validity of the mean-field approach for order-disorder phase transitions.

Cu-Au alloys represent almost all wide spectra of properties of alloys, including order-disorder phase transitions, formation of modulated structures, absence of miscibility gap, dependence of ordering on the vacancies concentration in an alloy, etc. [1-7]. This system appears to be a testing one for different approaches and models, that are aimed to describe phase relations in alloys. The most straightforward model for *ab initio* calculations is based on the Ising model with parameters obtained from first-principles band structure calculations [8-10]. The Monte Carlo simulations and the cluster variation method describe the main features of the equilibrium phase diagram in a proper way. At the same time the improvement of the statistical model does not help if one wishes to test the theory on more delicate properties of Cu-Au alloys, such as formation of modulated structures or distortions of the lattice appearing in the ordering transitions. In Ref. [1] it was shown that the Landau theory derived from an alloy Hamiltonian based on the semiempirical non-self-consistent approach of cohesion in solids provides a good description of the order-disorder transformation for CuAu, Cu₃Au and CuAu₃. The achievement of the Landau theory carried out in Ref. [1] is the prediction of a modulated CuAuII structure in the temperature range between CuAuI and disordered phase. Thus it was demonstrated that even within the mean-field approximation all main aspects of the phase diagram may be captured. At the same time it was shown in Ref. [1] that the CuAuI phase appears through a diffusionless first-order transition.

In addition to the results obtained in the framework of this approach which show its efficiency we would like to suggest in this paper a direct experiment which may settle the

question whether this theory is applicable also to the description of kinetics of growth of the phases. Especially we will pay attention to the study of the temperature dependence of the velocity of movement of the interface boundary in CuAu. Herewith an attempt is made to evaluate this effect and to predict the trends in thermo-induced dynamics of the interphase boundaries. In recent years the kinetics of the diffusionless first-order phase transition has been studied successfully on the basis of the time-dependent Ginzburg-Landau model [11-13]. These investigations were applied to the ferroelectric phase transitions and showed that the thermo-induced motion of the interphase boundary between paraelectric and ferroelectric phases may be realized as a motion of the solitary wave.

The dynamics of the interphase boundary in first-order diffusionless phase transformation of ordering alloys may be investigated in terms of the time-dependent Ginzburg-Landau equation [14]. The application of this model to the metallic system assumes that the heat conductivity in alloys is high and the interphase boundary motion can be described under the condition of the heat equilibrium and the interphase boundary dynamics is entirely governed by the evolution of the long-range order parameter, η :

$$\dot{\eta} = -\Gamma \frac{\delta F}{\delta \eta} \quad (1)$$

where Γ is the Landau-Khalatnikov transport coefficient which sets the time scale of the relaxation process and is assumed to be only slightly dependent on a temperature [15]. In future we shall neglect this dependence. F is the Ginzburg-Landau functional of the total free energy

$$F[\eta(x, t)] = \int [f(\eta) + D \cdot \eta_x^2] dx, \quad (2)$$

where $f(\eta)$ is the free energy density for a uniform system undergoing a first-order phase transition

$$f(\eta) = \frac{1}{2}a\eta^2 - \frac{1}{4}b\eta^4 + \frac{1}{6}c\eta^6, \quad (3)$$

with positive coefficients b and c . D is the coefficient of the inhomogeneity term, coefficient a is temperature dependent and has the form $a = a^{(1)} \cdot (T - T_0)$. T_0 is the stability limit of the disordered phase.

Comparing Eq.(2) with that one used in Ref. [1] it may be concluded that in our study we omit the term proportional to η_{xx} in the free energy functional. The coefficient D associated with the gradient term which accounts the interfacial free energy contribution is necessarily positive otherwise a one-phase state would never be stable (see for example Ref. [16]). The higher gradient terms are usually included when the first gradient term occurs to become negative. This happens, for example, if the coefficient of this term is obtained for some transforming system by fitting to the appropriate phonon dispersion curve at low reciprocal vector, $\vec{q}$, values. In this case the next and following higher order strain gradient terms have to be included, until a positive valued term is reached. The discussion on this situation is given in Ref. [17]. We will further preserve only linear gradient term and redetermine this term in a special manner, considering including the second term, $\sim \eta_{xx}^2$, asymptotically. Such a determination, as it will be shown later, sets up the additional temperature dependence of D .

We have several reasons to use such an asymptotic determination for the gradient term. 1. In Ref. [1] the term proportional η_{xx}^2 is competing with the term proportional to η_x^2 and it is responsible in this way for the formation of modulated structure. The period of modulation for CuAuII is rather large, $2M \sim 10d$ [18] (d is the lattice parameter). Thus we may assume that the antiphase structure does not affect sufficiently the process under investigation. 2. The temperature interval, ΔT , of existence of CuAuII structure is relatively small (for stoichiometric composition $\Delta T \propto 16K$). So the difference of the formation energies of CuAuII and CuAuI phases is also very small ($k\Delta T \propto 1.4 \cdot 10^{-3} eV$). Thus it is difficult to believe that the energy contribution of antiphase boundaries will change significantly the predictions of the kinetics of order-disorder phase transformation. 3. We are going to investigate a simple analytical soliton solution of the kinetic equation (1). 4. The results that will be obtained in our solution are applicable to other phases where the diffusionless first-order phase transformation is observed but it is not accompanied by the formation of antiphase boundaries.

Taking the enumerated circumstances into consideration we obtain the equation of motion that has the usual form of the time-dependent Ginzburg-Landau equation describing the motion of the interphase boundary (see also Refs. [19]).

$$2\Gamma D\eta_{xx} - \dot{\eta} - \Gamma(a\eta - b\eta^3 + c\eta^5) = 0 \quad (4)$$

This equation is the mean-field representation of the nonequilibrium interphase boundary kinetics. For a steady-state solution of Eq.(4) the profile of the long-range order parameter η is time independent, i. e. letting $s = x - vt$ and substituting the variable x by s we get:

$$2\Gamma D\eta'' + v\eta' - \Gamma(a\eta - b\eta^3 + c\eta^5) = 0 \quad (5)$$

The solution of Eq.(5) was discussed in Refs. [13]. The long-range order parameter has the kink form

$$\eta = \eta_0 \cdot \left(1 + \exp\left(\frac{s}{\Delta}\right)\right)^{-0.5} \quad (6)$$

where η_0 is the equilibrium value of the order parameter

$$\eta_0^2 = \frac{b}{2c} \left(1 + \sqrt{1 - \frac{4ac}{b^2}}\right) \quad (7)$$

and Δ is the width of the interphase boundary given by

$$\Delta = \frac{(3Dc)^{\frac{1}{2}}}{b\sqrt{1 - 2\alpha + \sqrt{1 - 4\alpha}}} \quad (8)$$

where $\alpha = ac/b^2$. This boundary moves with the velocity v , given by

$$v = \frac{\sqrt{2D}}{3} \frac{\Gamma b (8\alpha - 1 - \sqrt{1 - 4\alpha})}{\sqrt{c} \sqrt{1 - 2\alpha + \sqrt{1 - 4\alpha}}} \quad (9)$$

The solution (6) describes the propagation of the phase boundary leading to the phase transition.

Comparing the inhomogeneity terms of the Eq.(2) and of the Hamiltonian from the Ref. [1] the following relation may be justified

$$D \cdot \eta_x^2 = -|e| \cdot \eta_x^2 + |f| \cdot \eta_{xx}^2. \quad (10)$$

Here $|e|$ and $|f|$ are the gradient expansion coefficients, which are constants in the Ref. [1]. For the positive D the existence of the soliton solution in the form of Eq.(6) is proved. Substituting this solution into Eq.(10) and assuming reasonable asymptotic conditions $s \gg \Delta$, $s \sim \Delta$, and $s \ll \Delta$ we obtain

$$D = -|e| + |f| \cdot \frac{1}{\Delta^2} \cdot \begin{cases} 0.25, & s \gg \Delta, \\ 9.3 \cdot 10^{-3}, & s \sim \Delta, \\ 1, & s \ll \Delta. \end{cases} \quad (11)$$

The positivity of D is equivalent to the limitation of the width of the interphase boundary

$$\Delta \leq \sqrt{\frac{|f|}{|e|}} \cdot \begin{cases} 0.5, & s \gg \Delta, \\ 9.6 \cdot 10^{-2}, & s \sim \Delta, \\ 1, & s \ll \Delta. \end{cases} \quad (12)$$

For $CuAu$ using $|e|$ and $|f|$ values from Ref. [1] we obtain

$$\Delta \leq \begin{cases} 1.62 a.u., & s \gg \Delta, \\ 0.31 a.u., & s \sim \Delta, \\ 3.24 a.u., & s \ll \Delta. \end{cases}$$

These values of width may be observed for the planar interphase boundaries at the condition that the distance between different atomic layers is less than Δ . For $CuAu$, assuming a cubic symmetry, for the case $s \gg \Delta$ we get the following relation for the grain boundary indices $h^2 + k^2 + l^2 \geq 21$. From Eq.(11) D appears to be the temperature dependent and the Eq.(8) for Δ is transformed to

$$\Delta = \left[\left(\sqrt{|e|^2 + |f| \cdot \alpha_1^{-1}} - |e| \right) \cdot \alpha_1 \right]^{0.5} \cdot \begin{cases} 0.5, & s \gg \Delta, \\ 9.6 \cdot 10^{-2}, & s \sim \Delta, \\ 1, & s \ll \Delta. \end{cases} \quad (13)$$

where

$$\alpha_1 = \frac{3 \cdot c}{b^2(1 - 2\alpha + \sqrt{1 - 4\alpha})}.$$

The temperature interval of the existence of the steady-state solutions is determined by the relation $0 \leq \alpha \leq 1/4$. The dependence of the interphase boundary width Δ ($s \gg \Delta$) on the dimensionless temperature T/T_c at different overheating and overcooling temperatures is shown on the Fig.1.

Figure 1: The interphase boundary width Δ as a function of the dimensionless temperature T/T_c . The vertical line corresponds to $T = T_c$. The width is given in atomic units.

Here T_c is the temperature of the order-disorder phase transition. We used the data for T_0 from the Ref. [1] in our calculations. The parameters of the Ginzburg-Landau Hamiltonian are taken from the Ref. [1]. The calculated width of the boundary is in the interval $1.35 \div 1.55$ a.u. and it corresponds to the range of the existence of the steady-state solutions estimated earlier. The curve representing the dependence of the interphase boundary width on T/T_c grows slowly upto the transition temperature, T_c , and accelerates significantly just after the crossing T_c . The interval of overheating temperatures is four times smaller than the interval of overcooling temperatures. On the Fig.2 we have plotted the temperature dependence of the coefficient D (see Eq.(11), at the condition $s \gg \Delta$). D is positive and decreases with temperature in the range $(60kT \div 180kT)(a.u.)^2$. This result emphasizes that the change of D vs T is an important feature of the *CuAu* system. At the same asymptotic conditions the interphase boundary velocity v (Eq.9) in *CuAu* is plotted as a function of the dimensionless temperature T/T_c for the overcooling and overheating temperatures on Fig.3. The velocities are given in the units $\sqrt{2/c} \cdot \Gamma b/3$. We would like to note that the temperature for which the velocity is equal to zero (see Fig.3) corresponds to the equilibrium state of the interphase boundary and is the temperature of transition T_c . In this state the ordered and disordered phases are coexisting and the growth of phases is depressed.

The driving force of the interphase boundary movement is the tendency of the system to diminish its free energy through a kinetic relaxation towards equilibrium. From the point

of view of the interphase boundary kinetics for $s \rightarrow -\infty$ $\eta \rightarrow \eta_0$ and the ordered phase is obtained, for $s \rightarrow +\infty$ the disordered phase ($\eta = 0$) have to be observed.

Figure 2: The temperature dependence of the coefficient D of the inhomogeneity term in $kT \cdot (a.u.)^2$. The X-axis is the dimensionless temperature T/T_c .

Figure 3: The interphase boundary velocity v as a function of the temperature T/T_c for the overheating and overcooling intervals. The velocity is given in units of $\sqrt{2/c} \cdot \Gamma b/3$.

Simultaneous substitution x by $-x$ and v by $-v$ gives the antikink solution instead of the kink solution. This antikink solution presents a movement of the boundary with the opposite velocity, i. e. for the antikink we obtain $\exp(-\frac{x}{\Delta})$ in Eq.(6). Consequently, the moving interphase boundary separating the ordered and disordered phases is described by Eq.(6). According to Eq.(6) the disordered phase is located at the right, and the ordered

phase is situated at the left. The negative sign reverses this situation and puts the disordered phase at the left. Eq.(6) admits a multitude of particular solutions. We restricted herewith by steady-state solutions, where the interphase boundary moves with a constant velocity, v , given by Eq.(9). This means that the shape of the boundary does not change while moving. The first-order phase transition proceeds at a finite rate by means of the phase transition front which separates stable and metastable regions of the crystal specimen. The fixed interphase boundary shape is expected for a nonconserved order parameter. The interphase boundary preserves its shape during the propagation because of the competition of the two terms: the homogeneous part of the free energy density tends to bring the system to a stable state, while the inhomogeneous part of Eq.(2) has the opposite tendency. Under isobaric conditions, we can rewrite Eq.(9) as follows [13]

$$v = 2\Gamma[D a^{(1)}(T_c - T_0)]^{\frac{1}{2}} \frac{[\delta - \frac{2}{3}(1 + \sqrt{1 - \frac{3}{4}\delta})]}{\sqrt{1 - \frac{3}{8}\delta} + \sqrt{1 - \frac{3}{4}\delta}} \quad (14)$$

$$\delta = \frac{T - T_0}{T_c - T_0}, 0 \geq \delta \geq \frac{4}{3}. \quad (15)$$

It is seen that the interphase boundary velocity may be positive or negative depending on whether $T < T_c$ or $T > T_c$. The velocity v is therefore a function of overcooling and overheating. Analyzing the deviations from the linear dependence on the temperature of the interphase velocity we obtain by least squares fitting procedure for $T > T_c$ $v \propto (T - T_c)^n$, where $n = 0.988 \pm 0.002$, and for $T < T_c$ $v \propto (T_c - T)^m$, where $m = 1.028 \pm 0.002$. Thus the interphase boundary velocity is expressed in terms of the superheating and supercooling with the help of simple power laws. Although $v(T)$ seems to be a straight line the values n and m confirm the slight negative curvature of the v vs T dependence. This result is different from the boundary velocity behaviour obtained for the temperature-induced kinetics of the ferroelectric phase transitions in perovskites [13].

The surface tension of the interphase boundary σ is an additional free energy per unit area

$$\sigma = \int_{-\infty}^{+\infty} \left(\frac{\partial P}{\partial x} \right)^2 dx. \quad (16)$$

Using Eq.(6) and integrating in Eq.(16) we obtain

$$\sigma = \frac{D\eta_0^2}{4\Delta} \quad (17)$$

Using $D = 3.35 \cdot 10^{-16} \text{ cm}^2$ [18] and Eq. (9) we obtain $\sigma = 0.282 \frac{\text{erg}}{\text{cm}^2}$ at the same temperature ($T = T_c$ or $\alpha_c = \frac{3}{16}$). It is possible to check our calculations comparing with the experimental value for the surface tension of the interphase boundary for CuAu at $T = T_c$. This would be an additional evidence that the mean-field approximation works well in this case. Using (7), (11) and (17) we have

$$\sigma = \frac{b(1 + \sqrt{1 - 4\alpha})}{8c\Delta} \cdot \left[-|e| + |f| \cdot \frac{1}{\Delta^2} \cdot \begin{cases} 0.25, & s \gg \Delta, \\ 9.3 \cdot 10^{-3}, & s \sim \Delta, \\ 1, & s \ll \Delta. \end{cases} \right] \quad (18)$$

It is seen that the surface tension is a function of the boundary width and has different behaviour at different asymptotic conditions. In Fig. 4 the surface tension of the interphase boundary σ is shown at different asymptotics.

Figure 4: The surface tension σ as a function of the dimensionless temperature T/T_c . The vertical line corresponds to $T = T_c$. σ is given in b/c units. The lower and upper curves correspond to upper and lower limits of Eq.(18) respectively.

The decreasing tendency takes place in the two cases. The upper curve describes the case $s \gg \Delta$ and the lower curve corresponds to $s \ll \Delta$. It is seen that the surface tension is a increasing function of T . These T dependences of σ are described by the corresponding behaviour of the interphase boundary width following from (7) and (12).

We expect that one of the ways of justifying the atomistic Landau theory for the CuAu order-disorder phase transition may be carried out through kinetics experiments on the phase growth. The interphase boundaries may be observed in the polarization microscope. The possibility to measure the velocity of these boundaries at different temperatures would present a direct provement of the applicability of the mean-field approach to this type of phase transitions. The indirect information on the kinetics of growth of disordered phase when overheating may be obtained by the measurements of electric resistivity of samples. Analogous effects are well-known and the application of the theory to ferroelectric perovskites was proved by experimental facts [20-22].

This work was supported in the part by Israel Ministry of Science, Grant 4868, and by Israel Ministry of Absorption under the special program for the science absorption. One of us (D.F.) is thankful to the Rashi Foundation for support. The support of the Technion - Haifa University Foundation is appreciated.

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