Manifestation of the Fermi surface in phase transitions of metallic alloys

N. M. Dunaev and M. I. Zakharova

Moscow State University
(Submitted July 2, 1974)
ZhETF Pis. Red. **20**, No. 11, 726–730 (December 5, 1974)

The possibility of the appearance of a singularity in the band-structure spectrum of a nonequilibrium alloy is demonstrated. This singularity is connected with the Fermi surface and is manifest in the appearance of modulation of the concentration.

Binary solid solutions of metals in which the solubility of the second component decreases with decreasing temperature become supersaturated and unstable if they are abruptly cooled from high temperatures. When isothermally maintained, such nonequilibrium solutions become unstable relative to fluctuations of the concentration of the components of certain wavelengths.

The solid-solution model describes the initial stages of the phase transition with the aid of the mutual-diffusion spectral coefficient[1–3]:

$$D_q = D[1 + 2\kappa B_q^2 /(f'' + 2\eta^2 Y + E_q)].$$ (1)

Here D is the mutual-diffusion coefficient measured at macroscopic distances; Y is the effective modulus of elasticity and is a slowly varying function of the wave vector q of the concentration fluctuations; $\eta = (da/dc)/a$, where a is the lattice parameter of the alloy and c is the alloy concentration; f'' is the second derivative of the free-energy density with respect to the concentration; $B_q^2 = (8/a^2)[1 - \cos(ka/2)]$ for the $\langle 100 \rangle$ directions in cubic structures; κ is a coefficient; E_q is the singular part of the second derivative of the energy density of the band structure with respect to the concentration. We propose to introduce this term to take into account the contribution made to the total energy of the alloy by the energy gaps due to the formation of a concentration-modulated structure. The order of magnitude of this term is 10^{-2} of the elastic-energy density $2\eta^2 Y$, so that it can usually be disregarded. For nonequilibrium solid solutions near the coherent spinodal, however, when $f'' + 2\eta^2 Y = 0$, the term E_q, plays a decisive role, in view of its singular character. The singularities of E_q result from the singularity of the screening of the interaction between the ions, when the wave quasivector of the concentration fluctuation satisfies the condition that $g \pm q$ be equal to $2K_F$, i.e., to an extremal diameter of the Fermi surface of the alloy in the given direction. Here g is the reciprocal-lattice vector.

Calculations based on the pseudopotential theory yield for the singular part E_q

$$E_q = -2N |2k_F A_q|^2 [(2K_F)^2 /8\pi e^2]_i < K + 2K_F | c w^{(2)}$$
$$+ (1 - c)w^{(1)} |K>|^2$$ (2)
$$\times \frac{\epsilon(2K_F) - 1}{\epsilon(2K_F)}.$$

Here is the dielectric constant, N is the number of lattice sites per cm³ of the alloy, $\langle K + 2K_F | c w^{(2)} + (1 - c)w^{(1)}|K\rangle$ is the form factor of the alloy at $q = g - 2K_F$, and

$$A_q = \frac{1}{2} a\eta \frac{c_{11} + 2c_{12}}{c_{11}} \text{ctg}(qa/4)\mathbf{n},$$ (3)

where c_{ij} are the elasticity matrix elements. In symmetrical directions we have $\mathbf{n} = \mathbf{q}/|\mathbf{q}|$.

Since $\epsilon(2K_F) - 1$ in formula (2) is proportional to the density of states on the Fermi surface, the jump of the spectral mutual-diffusion coefficient D_q as a function of the concentration-fluctuation wave vector q will be maximal for transition-metal alloys, especially those having a flat section of the Fermi surface.

We assume that in the case of isothermal soaking of a supersaturated solution of Ni in Au at temperatures ~150 °C, when modulation of the concentration is observed with a wavelength $\lambda = 17.1$ Å at $C_{Ni} = 0.2$ to $\lambda = 6.5$ Å at $C_{Ni} = 0.54$ in the $\langle 100 \rangle$ direction,[4,5] a jump of D_q appears (Fig. 1) and as a result, for all the wave

FIG. 1.

FIG. 2.
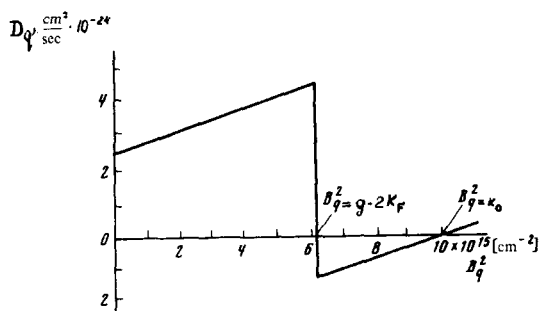
numbers q satisfying the condition

$$2K_F \leqslant g - q < K_o \quad , \tag{4}$$

the spectral mutual-diffusion coefficient D_q is negative. This means that concentration fluctuations with these wave vectors will not decrease with time, as in the case $D_q > 0$, but increase. At first, before the nonlinear effects come into play, the amplitude of these concentration waves increases with time in accordance with the law

$$C_q(t) = C_q(0) \exp(pt) \cos(qr), \tag{5}$$

where

$$p = - D_q B_q^2 \quad . \tag{6}$$

Owing to the exponential growth of the amplitudes (5), the only concentration-fluctuation wavelength that becomes experimentally noticeable is the one for which the diffusion coefficient D_q is negative and minimal; this occurs, as seen from Fig. 1 and condition (4), at $q = g$ $- 2K_F$. Thus, the singularity connected with the extremal diameter of the Fermi surface of the alloy at q $= g - 2K_F$ becomes experimentally manifest in the Au-Ni alloy in the form of modulation of the concentration, with wavelength $\lambda = 2\pi/q$. For each given average solution concentration, the extremal diameter of the Fermi surface of the alloy remains practically unchanged with temperature in the region 0—200 °C. This was indeed observed in experiments[5] in the form of independence of the concentration-modulation wavelength as temperature was increased from 0 to 220 °C, in contradiction to the theory of spinodal decay, [6] which calls for the wavelength of the modulation to increase with temperature. Experiment, in addition, contradicts the theory of spinodal decay also with respect to the temperature region, revealing a modulated structure of the Au-Ni alloy at a temperature 220 °C higher[5] than predicted by calculation in accordance with this theory. [7]

For the concentration $C_{Ni} = 0.46$ we have $\lambda = 7$ Å, and to explain the experimental data it is necessary to have $E_q \approx - 2 \times 10^{10}$ erg/cm^3. An estimate of E_q in accordance with formula (2) yields $E_q \approx - 5 \times 10^{10}$ erg/cm^3.
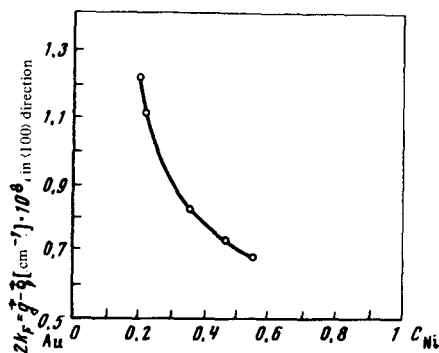
A singularity of E_q, in the form of a "decrease," ap-

pears in the process with umklapp, when an electron with wave vector $\mathbf{K}$ is diffracted by a concentration wave with wave vector $\mathbf{q}$ and goes over a position with wave vector $\mathbf{K} - \mathbf{g} - \mathbf{q}$. The value of $\mathbf{q}$ corresponds in this case to the smallest distance between the Fermi surfaces in the $\langle 100 \rangle$ direction in the expanded-band scheme. Consequently, by determining from experiment[4,5] the concentration-modulation wavelength λ, we calculate the extremal diameter of the Fermi surface of the Au-Ni alloy in the $\langle 100 \rangle$ direction by means of the simple formula

$$2K_F = g - 2\pi/\lambda \quad . \tag{7}$$

Figure 2 shows the extremal diameter of the Fermi surface of the AU-Ni alloy in the $\langle 100 \rangle$ direction, calculated in accordance with formula (7).

The decrease of K_F, and consequently of the Fermi level in Au following addition of Ni can be explained qualitatively as being due to a decrease $|S|$ of the charge at Au, [8] which is offset by the formation of a new d-subband, just as in the Cu-Ni alloy. [9] A possible reason why an appreciable lowering of the Fermi level in the Au-Ni alloy begins only at $C_{Ni} \geqslant 20$ at.% may be that at lower Ni concentrations the perturbation due to the replacement of the Au atom by the Ni atom is localized around the Ni impurity. [10]

[1]H.E. Cook, D. de Fontain, and J.E. Hilliard, Acta Met. 17, 765 (1969).

[2]H.E. Cook and J.E. Hilliard, J. Appl. Phys. 40, 2191 (1969).

[3]H.E. Cook and D. de Fontain, Acta Met. 19, 607 (1971).

[4]Y. Fukano, J. Phys. Soc. Japan 16, 1195 (1961).

[5]J.E. Woodilla and B.N. Averbach, Acta Met. 16, 255 (1968).

[6]J.W. Cahn, Acta Met. 9, 795 (1961); 10, 179 (1962).

[7]B. Golding and S.C. Moss, Acta Met. 15, 1239 (1967).

[8]R.E. Watson, J. Hudis, and M.L. Perman, Phys. Rev. B 4, 4300 (1971).

[9]G.M. Stocks, R.W. Williams, and J.S. Faulkner, Phys. Rev. B4, 4390 (1971).

[10]E. Stern, Phys. Rev. B: Solid State 5, 366 (1972).