Concentration Dependence of the Spin-Density-Wave Periodicity in Antiferromagnetic Chromium Alloys

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The dependence of the periodicity of the spin-density waves in antiferromagnetic metals upon the number of conduction electrons is studied theoretically. It is seen that the commensurable structure, i.e., the structure for which the wave vector q equals half a reciprocal lattice vector G, is the state of minimum energy over a finite range of electron densities. The effect, which has been observed experimentally, is essentially due to the presence of two energy gaps which coalesce into one in the commensurable state. The theory gives quantitative relationships which are in good agreement with the experimentally determined values for the chromium-rich Cr-Mn and Cr-Re alloys.

I. INTRODUCTION

THE occurrence of antiferromagnetism in metallic chromium and its alloys has been satisfactorily explained in terms of spin-density waves (SDW).[1-7] This theory assumes that itinerant electrons in a metal are strongly correlated in such a way that there is at least one nonzero oscillatory component of the magnetization M_q. Each component M_q is characterized by an amplitude M_q, a wave vector q, and a polarization. These properties have all been determined experimentally by means of neutron diffraction.[8-14]

The self-consistent SDW theory[2,5] shows that the excitation spectrum of the electrons in such a system exhibits energy gaps. If the paramagnetic spectrum of the electrons is described by a band structure $\epsilon(\mathbf{k})$, the antiferromagnetic energy gaps appear whenever the condition

$$\epsilon(\mathbf{k}) = \epsilon(\mathbf{k} + n\mathbf{q}) \qquad (1.1)$$

is satisfied; in (1.1) n is any nonzero integer. It has been proven experimentally[15] and theoretically[16] that values of the gaps with $n \neq \pm 1$ are in general very small and can be neglected; consequently (1.1) can be reduced to

$$\epsilon(\mathbf{k}) = \epsilon(\mathbf{k} \pm \mathbf{q}). \qquad (1.2)$$

The magnitude of these antiferromagnetic gaps[5] is proportional to M_q. Stability arguments[5,17] also show that the value of the $\mathbf{q}$ vector is such that the appearance of energy gaps results in the annihilation of a sizeable portion of the paramagnetic Fermi surface. That is, the $\mathbf{q}$ vector should connect two rather "flat" pieces of Fermi surface which run nearly parallel to each other. In this respect, the problem can be considered in essence a one-dimensional one, since the band structure changes appreciably only in a direction normal to the Fermi surface, or equivalently, normal to the surface defined by (1.2). In the case of pure chromium, $\mathbf{q}$ takes the value

$$\mathbf{q} = \pm (2\pi/a)(1 - \delta_0, 0, 0), \qquad (1.3)$$

where δ_0 is a temperature-dependent small quantity which varies approximately between 0.05 and 0.035. It should be remembered that the presence of a crystal lattice makes $\mathbf{q} + \mathbf{G}$ ($\mathbf{G}$ any reciprocal lattice vector) an equivalent representation of $\mathbf{q}$; consequently the SDW vector can also be defined, for instance, by

$$\mathbf{q}^* = \pm (2\pi/a)(1 + \delta_0, 0, 0) \qquad (1.4)$$

as well as many other possible values.

The stability criterion quoted above has been used to relate the values (1.3) and (1.4) to the features of the Fermi surface of chromium,[18] and it is seen in Fig. 1 that in fact $\mathbf{q}$ connects, as expected, two "flat" pieces

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of Fermi surface, the so-called hole "octahedron" and electron "jack."

The relationship between $\mathbf{q}$ vector and Fermi surface is more explicitly shown by the experimentally determined change of $\mathbf{q}$ upon alloying.[17,19,20] The addition of a small concentration of vanadium, which is to the left of chromium in the periodic table, lowers the value of the Fermi energy of the system with a consequent enlargement of the hole octahedron and a reduction of the electron jack; as expected (see Fig. 1) the $\mathbf{q}$ vector changes so that δ increases from its δ_0 values with increasing V concentration. The alloying of a few percent of tungsten into chromium, which leaves the total number of conduction electrons unchanged, produces a very small increase in δ; this increase on the whole is smaller than the change in δ_0 with temperature. Finally the alloying of manganese or rhenium, both with one more conduction electron than chromium, produces an effect just opposite to that of V.

In this last case, however, more interesting effects appear. For alloys more concentrated than about 1.5% Re or Mn, the magnetic structure of the alloy becomes commensurable with the crystal lattice at all temperatures above 4.2°K, i.e., δ is identically zero and $\mathbf{q}$ is then equal to exactly half a reciprocal lattice vector. For alloys with smaller concentration of the impurity two structures are observed: a low-temperature structure (called O in Ref. 17) with nonvanishing δ, which is nonetheless smaller than that of pure chromium δ_0, and a high-temperature structure C, commensurable with the crystal lattice, in which $\delta = 0$. The phase transition C-O takes place at a temperature T_{CO} which decreases rapidly with increasing concentration; the phase transition shows temperature hysteresis. In all these cases it is found that as the concentration of the impurity increases and δ decreases the value of the magnetization intensity increases by about a factor of 2 in the range 0–7 at.% of the diluent.[17]

Several features of these experiments need explanation: (1) Why, if the $\mathbf{q}$ vector tends to follow the Fermi surface, δ jumps abruptly from a finite value to $\delta = 0$ and why it gets locked in at that value? (2) Why and how a phase transition takes place?

We present here a theory which yields an explanation for these effects and which provides numerical correlations between various quantities measured experimentally. The presentation of the theory will be divided into four parts: (a) classification of the electron states in the antiferromagnetic metal; (b) calculation of the antiferromagnetic band structure; (c) calculation of the total energy of the antiferromagnetic bands; and (d) minimization of the total energy and discussion of phase stability.

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[20] As found by Koehler et al. (Ref. 17), V_q increases by a factor two upon the addition of 6% Mn to Cr. This change of V_i with ϵ_i will also contribute to E_i, but we neglect this effect for simplicity.
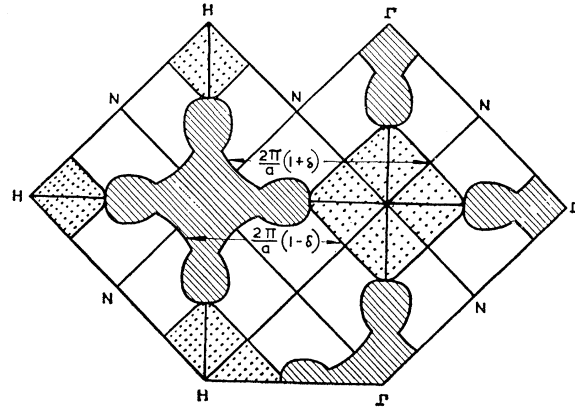

FIG. 1. Cross section of the Fermi surface of Cr in the (100) plane. The shaded area represents the electron jack and the dotted surface represents the hole octahedron. The vectors with magnitude $q = (2\pi/a)(1 \pm \delta)$ which connect the two pieces of Fermi surface are indicated.

II. THEORY

A. Electrons in an Antiferromagnetic Metal

We may consider the electronic system in pure Cr or in the Cr-rich alloys divided into two parts:

(a) an antiferromagnetic d-band part, which includes only those electrons whose Fermi surface is annihilated by the antiferromagnetic interaction;

(b) the rest of the (s- and d-like) conduction electrons, whose band structure is modified by the antiferromagnetic interaction but whose Fermi surface is left essentially unchanged. This last part is referred to in this paper as the reservoir.

The total number N of conduction electrons in the metal can thus be written as

$$N = N_{A0} + N_{A1} + N_B, \qquad (2.1)$$

where N_{A0} is the number of electrons in A when no excitations are present, N_{A1} is the (positive, zero, or negative) number of electrons in excited states in A, and N_B is the number of electrons in the reservoir. Each of these groups contribute to the total energy (or free energy) of the system. At $T = 0$, if we neglect the excitations, i.e., $N_{A1} = 0$, the total energy E_T can be rewritten as

$$E_T = E_{TA} + E_{TB}, \qquad (2.2)$$

where the terms on the right-hand side of (2.2) are the ground-state energies of A and B.

If for the reservoir we take an independent quasiparticle model, the total energy E_{TB} depends only on the Fermi energy ϵ_F of the reservoir, and is such that

$$dE_{TB} = \epsilon_F \rho(\epsilon_F) d\epsilon_F. \qquad (2.3)$$

The number of electrons in the reservoir varies accordingly, so that

$$dN_B = \rho(\epsilon_F) d\epsilon_F. \qquad (2.4)$$

In (2.3) and (2.4), $\rho(\epsilon_F)$ is the density of states at the Fermi surface; this quantity is measured experimentally by means of, e.g., electronic-specific-heat measurements.

It should be remembered that the A part of the systems exhibits no free Fermi surface and consequently gives no contribution to the electronic specific heat.

The calculation of N_{A0} and E_{TA} requires a determination of the details of the antiferromagnetic band structure.

B. Antiferromagnetic Band Structure

In the absence of excitations, the SDW theory shows that the system A (essentially a one-dimensional one) is such that the one-electron spectrum exhibits an energy gap right at the Fermi energy. That means that condition (1.2) is satisfied for

$$\epsilon_1(\mathbf{k}) = \epsilon_2(\mathbf{k+q}) = \epsilon_a, \qquad (2.5)$$

where the subscripts 1 and 2 indicate that the two paramagnetic bands are not necessarily the same and $\epsilon_a \approx \epsilon_F$. In addition, as Fig. 2 shows, the fact that $\delta \neq 0$ implies that another gap of the same order of magnitude should be present in a region in k space quite close to the (destroyed) paramagnetic Fermi surface. This second gap appears at values of $\mathbf{k}$ such that

$$\epsilon_1(\mathbf{k}) = \epsilon_2(\mathbf{k+q^*}) = \epsilon_d, \qquad (2.6)$$

where $\mathbf{q^*}$ is given by (1.4). In Cr and its alloys,

$$\epsilon_d > \epsilon_a. \qquad (2.7)$$

It is important to emphasize at this point that the energy gaps tend to follow the electron distribution. The addition of extra electrons to the system decreases δ and changes the value of ϵ_a and ϵ_d, and the two energy gaps coalesce into one.

The antiferromagnetic band structure can be obtained[5] by solving an infinite-order secular equation of the form

$$
\begin{vmatrix}
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\
& \cdot & \cdot & \cdot & \cdot & \cdot & \\
\epsilon(\mathbf{k+q^*-q})-\lambda & V_q & 0 & 0 & 0 & \cdots \\
\cdots & V_q & \epsilon(\mathbf{k+q^*})-\lambda & V_q & 0 & 0 & \cdots \\
\cdots & 0 & V_q & \epsilon(\mathbf{k})-\lambda & V_q & 0 & \cdots \\
\cdots & 0 & 0 & V_q & \epsilon(\mathbf{k+q})-\lambda & V_q & \cdots \\
\cdots & 0 & 0 & 0 & V_q & \epsilon(\mathbf{k+q-q^*})-\lambda \\
& \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
& \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
& \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
\end{vmatrix} = 0, \qquad (2.8)
$$

where for the sake of simplicity we may take

$$V_q = V_q^*(\text{real}). \qquad (2.9)$$

When $\delta = 0$, (2.8) is replaced by a 2×2 secular equation

$$
\begin{vmatrix}
\epsilon(\mathbf{k})-\lambda & V_0 \\
V_0 & \epsilon(\mathbf{k+G}/2)-\lambda
\end{vmatrix} = 0. \qquad (2.10)
$$

In (2.8) and (2.10) the off-diagonal matrix elements V_q and V_0 are proportional to the amplitude of the magnetization waves M_q and $M_{G/2}$, respectively.

If the eigenvalues λ of either (2.8) or (2.10) are designated by $E(\mathbf{k})$, the total energy of the system E_{TA} is given by[5]

$$E_{TA} = \sum_{\mathbf{k},\text{occupied states}} E(\mathbf{k}) + \sum_q |V_q|^2 N/C_0, \qquad (2.11)$$

where N is the number of atoms in the crystal, C_0 is an electron-electron interaction strength, and the sum-

mation over $\mathbf{q}$ includes all those values of SDW vectors in the first Brillouin zone of the paramagnetic structure. Continuity of (2.11) as $\mathbf{q} \rightarrow \frac{1}{2}\mathbf{G}$ as well as continuity of (2.8) into (2.10) requires that

$$\lim_{q \to G/2} V_q = V_0/\sqrt{2}. \qquad (2.12)$$

This equation indicates that the root mean square of the magnetization is continuous, although the maximum value of $\mathbf{M}$ is not.[17]

Solutions of (2.8) exhibit an infinite number of gaps, as predicted by (1.1). If we only retain first-order gaps, the band structure has the general form shown in Fig. 2(B). The following features can be obtained from a detailed analysis of (2.8):

(i) Two energy gaps

$$E_g = E_b - E_a \cong E_d - E_c, \qquad (2.13)$$

are present in the spectrum, and correspond to unperturbed energies ϵ_a and ϵ_d given by (2.6) and (2.7).
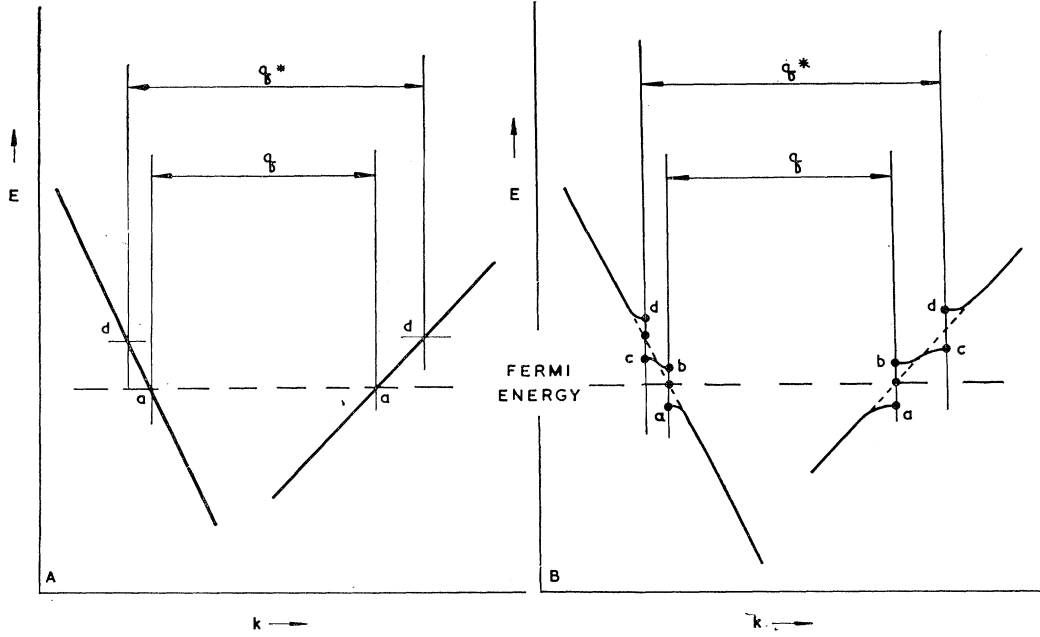
FIG. 2. (A) Hypothetical band structure in the absence of antiferromagnetism. (B) Modification of the energy
bands in the presence of a SDW state of wave vector q.

(ii) E_g takes the following limiting values:

$$E_g = 2V_q, \qquad \delta \text{ very large}$$

$$= \sqrt{2}\, V_q, \qquad \delta \to 0. \qquad (2.14)$$

(iii) The energy gap at $\delta = 0$ is

$$E_G = E_d - E_a = 2V_0 = \lim_{q \to G/2} 2\sqrt{2}\, V_q, \qquad (2.15)$$

since in this case the intermediate band [b-c in Fig
2(B)] does not exist.

If, for the sake of definiteness, we assume that the
two connected pieces of Fermi surface have equal and
opposite velocities and that the zero of energy is taken
at the point

$$\epsilon_1(\mathbf{k}_0) = \epsilon_2(\mathbf{k}_0 + \tfrac{1}{2}\mathbf{G}) = 0, \qquad (2.16)$$

then we can write

$$\epsilon_1(\mathbf{k}) = -\epsilon_2(\mathbf{k} + \tfrac{1}{2}\mathbf{G}) = \epsilon(\mathbf{k}), \qquad (2.17)$$

and the following results are found:

(1) At $\delta = 0$ the bands are given by

$$E(\mathbf{k}) = \pm \{ [\epsilon(\mathbf{k})]^2 + V_0^2 \}^{1/2}. \qquad (2.18)$$

(2) As δ becomes very large the lower band is given
by

$$E(\mathbf{k}) = \epsilon(\mathbf{k}_a) - \{ [\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}_a)]^2 + V_q^2 \}^{1/2}, \qquad (2.19)$$

where

$$\epsilon(\mathbf{k}_a) = \epsilon(\mathbf{k}_a + \mathbf{q}) = \epsilon_a, \qquad (2.20)$$

and

$$E(\mathbf{k}_a) = \epsilon(\mathbf{k}_a) - |V_q|. \qquad (2.21)$$

It is important for our purposes to find analytic
expressions for the lower and upper bands. From the

discussion above it can be seen that, for the lower
band,

$$E(\mathbf{k}) = \epsilon_a - \{ [\epsilon(\mathbf{k}) - \epsilon_a]^2 + \Delta_a^2 \} \qquad (2.22)$$

gives the correct limiting behavior at both very large
and very small δ. In (2.22) ϵ_a is defined by (2.20) and

$$\Delta_a(\delta) = \epsilon_a - E_a \qquad (2.23)$$

should satisfy the following conditions:

$$\Delta_a(\delta = 0) = V_0 = \lim_{q \to G/2} \sqrt{2}\, V_q, \qquad (2.24)$$

$$d\Delta_a/d\epsilon_a \mid_{\delta=0} = -1, \qquad (2.25)$$

$$\lim_{\delta \to \infty} \Delta_a = V_q + O(V_q^2/\epsilon_a). \qquad (2.26)$$

These conditions are satisfied by an expression of the
form

$$\Delta_a = V_q + \epsilon_a + [\epsilon_a^2 + \alpha^2 V_q^2]^{1/2}, \qquad (2.27)$$

where

$$\alpha = \sqrt{2} - 1. \qquad (2.28)$$

Corresponding expressions can be written for the upper
band.

C. Total Energy of the Antiferromagnetic Band

We now calculate the change in the total energy
E_{TA} [Eq. (2.11)] with the number of electrons N_{A0},
i.e.,

$$E_s = \delta E_{TA}/\delta N_{A0}. \qquad (2.29)$$

We call E_s the separation energy, and in varying the
number of electrons we always keep the antiferro-
magnetic system in its ground state. This means that
the occupation of the one-particle states is such that

(i) if N_{A0} is less than N_{AC} (the number in the commensurable state $\delta=0$), all states up to E_a are filled, the second and third bands remaining empty [see Fig. 2(B)]; (ii) if N_{A0} is greater than N_{AC}, all states up to E_c are filled while the third band is completely empty.

It is evident that the problem has symmetry about the $N_{A0}=N_{AC}$ value, but that the separation energy should be discontinuous at $N_{A0}=N_{AC}$, i.e., at $\epsilon_a=\epsilon_d=0$. For $N_{A0}<N_{AC}$ with the occupation numbers completely defined, E_{TA} is only a function of two independent variables ϵ_a and V_q. Consequently

$$E_s=\frac{\partial E_{TA}}{\partial \epsilon_a}\frac{d\epsilon_a}{dN_{A0}}+\frac{\partial E_{TA}}{\partial V_q}\frac{dV_q}{dN_{A0}}. \qquad (2.30)$$

However, the equilibrium condition which minimizes the total energy for a fixed number of electrons implies

$$\partial E_{TA}/\partial V_q=0, \qquad (2.31)$$

and the calculation of the separation energy requires only the calculation of the first term in (2.30).

We can write, to a very good approximation,

$$\frac{d\epsilon_a}{dN_{A0}}\equiv K=\frac{\hbar v_F}{S_F}\frac{(2\pi)^3}{2\Omega}, \qquad (2.32)$$

where v_F is the Fermi velocity in the relevant d band of the paramagnetic structure, S_F is the area of the destroyed portion of the Fermi surface, and Ω is the volume of the sample.

The calculation of $\partial E_{TA}/\partial \epsilon_a$ proceeds as follows:

$$\frac{\partial E_{TA}}{\partial \epsilon_a}=\frac{\partial}{\partial \epsilon_a}\Big[\sum_{\mathbf{k},\text{occupied states}} E(\mathbf{k})\Big]$$

$$=\frac{\partial}{\partial \epsilon_a}\Big[\int^{\epsilon_a} E(\epsilon,\epsilon_a)\mathfrak{N}(\epsilon)\,d\epsilon\Big]. \qquad (2.33)$$

If we take for $E(\epsilon,\epsilon_a)$ the approximate expression (2.22) and remember that the density of states $\mathfrak{N}(\epsilon)$ in (2.33) is given by

$$\mathfrak{N}(\epsilon_a)=dN_{A0}/d\epsilon_a=1/K, \qquad (2.34)$$

we obtain

$$E_s=\epsilon_a-\Delta_a(\partial\Delta_a/\partial\epsilon_a)\,\ln(2W_a/\Delta_a), \quad N_{A0}<N_{AC} \quad (2.35)$$

where W_a is an energy of the order of half the d bandwidth. Similarly

$$E_s=\epsilon_d+\Delta_d(\partial\Delta_d/\partial\epsilon_d)\,\ln(2W_d/\Delta_d), \quad N_{A0}>N_{AC}. \quad (2.36)$$

If for Δ_a (or Δ_d) we take an expression like (2.27), assume that V_q is a constant equal to its value for pure chromium[20,21]

$$V_q\cong0.03 \text{ eV}, \qquad (2.37)$$

and choose[22]

$$W_a=W_d\cong1.5 \text{ eV},$$

then a plot of Eqs. (2.35)–(2.36) is that shown in Fig. 3.

D. Total Energy and Phase Stability

To find the equilibrium configuration, i.e., the value of δ which minimizes the total energy, we impose the condition

$$dE_T=dE_{TA}+dE_{TB}=0 \qquad (2.38)$$

subject to the constraint of a constant number of electrons

$$dN=dN_{A0}+dN_B=0. \qquad (2.39)$$

It follows from Eqs. (2.3), (2.4), and (2.29)–(2.32) that these conditions are equivalent to

$$E_s=\epsilon_F. \qquad (2.40)$$

At the same time the total number of electrons is given by

$$N=N_G+\int_0^{\epsilon_F}\rho(\epsilon)\,d\epsilon+\int_0^{\epsilon_a,\epsilon_d}K^{-1}d\epsilon, \qquad (2.41)$$

where N_G is the number of electrons corresponding to the case $\epsilon_F=0$, $\epsilon_a=\epsilon_d=0$. Equation (2.41) yields for the Fermi energy

$$\epsilon_F=[\Delta N-(\epsilon_0/K)]/\rho(\epsilon_F), \qquad (2.42)$$

where ϵ_0 indicates either ϵ_a or ϵ_d, and

$$\Delta N=N-N_G. \qquad (2.43)$$

The extremal condition (2.40) requires that

$$E_s(\epsilon_a)\equiv\epsilon_a-\Delta_a(\partial\Delta_a/\partial\epsilon_a)\,\ln(2W_a/\Delta_a)$$

$$=\frac{\Delta N-(\epsilon_a/K)}{\rho(\epsilon_F)}\equiv\epsilon_F(\epsilon_a;\Delta N) \qquad (2.44)$$

for ΔN negative and

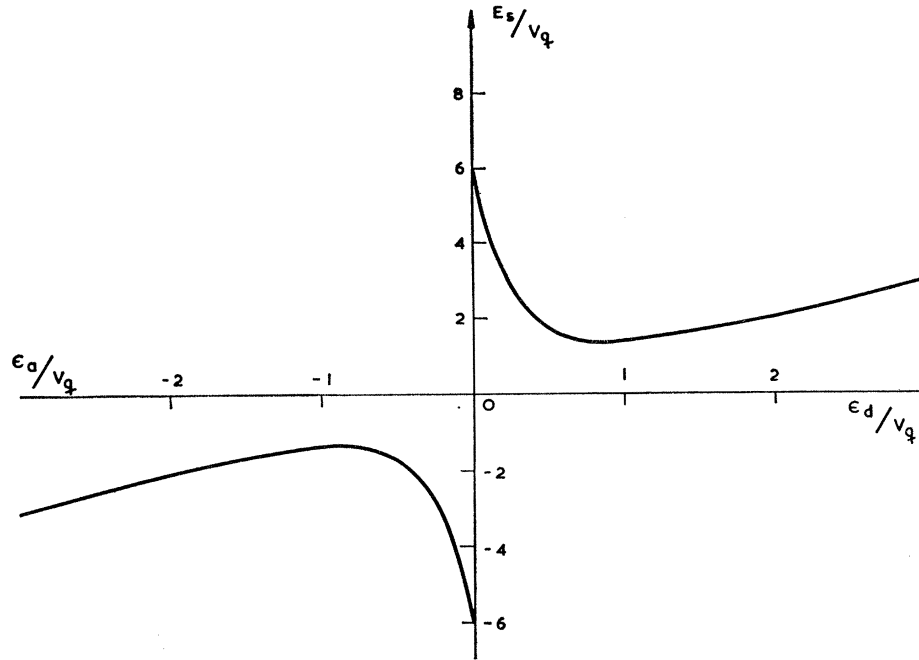$$E_s(\epsilon_d)=\epsilon_d+\Delta_d(\partial\Delta_d/\partial\epsilon_d)\,\ln(2W_d/\Delta_d)$$

$$=\frac{\Delta N-(\epsilon_d/K)}{\rho(\epsilon_F)}\equiv\epsilon_F(\epsilon_d;\Delta N) \qquad (2.45)$$

for ΔN positive.

The equilibrium values of ϵ_a (or ϵ_d) corresponding to a given ΔN are obtained graphically from the intersection of the curves $E_s(\epsilon_a)$ and $\epsilon_F(\epsilon_a;\Delta N)$ as illustrated in Fig. 4. The energy $\epsilon_F(\epsilon_a;\Delta N)$ is plotted for five values of ΔN, ΔN_1–ΔN_5; these go in increasing order. The value ΔN_1 corresponds approximately to pure Cr while the others refer to suitable Cr-Mn or Cr-Re alloys.

In Fig. 5 the total energy $E_T=E_{TA}+E_{TB}$ is shown schematically for each of the five values of ΔN. The stable or metastable equilibrium values of ϵ_a, ϵ_{ae} correspond to the minima in the E_T curve. As ΔN increases from ΔN_1, the only minimum in the curve, ϵ_{ae}, moves smoothly towards zero. At $\Delta N=\Delta N_2$ a second minimum appears at $\epsilon_a=0$. This is a local minimum at a

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FIG. 3. Plot of the separation energy E_s as a function of ϵ_a [Eqs. (2.33) and (2.36)].

point of slope discontinuity, i.e., a cusp. For ΔN between ΔN_2 and ΔN_3 the oscillatory structure and the commensurable one are both local minima, but O is still the stable one while C is metastable. For $\Delta N_3 < \Delta N < \Delta N_4$, C becomes the stable structure and O is only metastable. Finally for $\Delta N_4 < \Delta N < 0$ only one structure, C, satisfies the condition of being a minimum.

The equilibrium value of δ, δ_e is obtained from

$$\delta_e = \frac{2 \mid \epsilon_a \mid}{\hbar v_F \mid G \mid} = C_a \frac{\mid \epsilon_a \mid}{W_a}, \qquad \Delta N < 0 \qquad (2.46)$$

$$= \frac{2\epsilon_d}{\hbar v_F \mid G \mid} = C_d \frac{\epsilon_d}{W_d}, \qquad \Delta N > 0 \qquad (2.47)$$
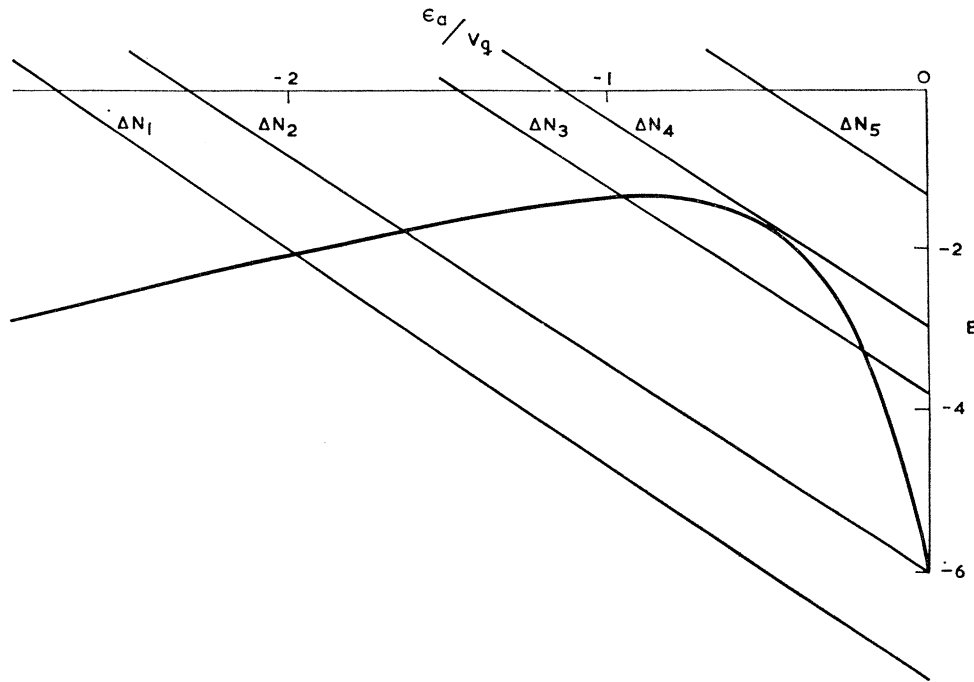
FIG. 4. Plot of the separation energy $E_s(\epsilon_a)$ and of the Fermi energy of the reservoir $\epsilon_F(\epsilon_a, \Delta N)$ [Eq. (2.44)] for five values of ΔN. The critical values of ϵ_a are determined from the intersections of the curves.
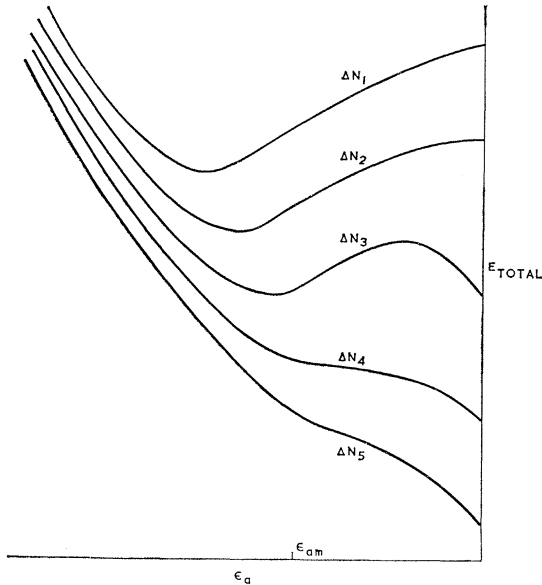
FIG. 5. Schematic plots of the total energy versus ϵ_a for the values of ΔN shown in Fig. 4. The equilibrium value of $\epsilon_a = \epsilon_{ae}$ corresponds to the minimum in the E_{total} curve. ϵ_{ae} is zero for $\Delta N > \Delta N_3$; ϵ_{am} is the maximum stable nonzero value of ϵ_{ae}.

where $|G|$ is $4\pi/a$, v_F is the Fermi velocity, C_a and C_d are numerical constants of the order of one, and W_a and W_d are the bandwidths used in Eqs. (2.35) and (2.36).

From Figs. 4 and 5 it is seen that δ_e has a minimum value δ_m corresponding to ΔN_3. This quantity can be obtained from the curves and it is a function of K, ρ, V_q, W_a, and C_a. We choose for these parameters the following range of reasonable values:

$$\rho \sim 1\text{-}2 \; [\text{eV atom}]^{-1} \quad (\text{Ref. 23}),$$

$$K\rho \sim 1\text{-}2,$$

$$V_q \sim 0.03\text{-}0.06 \; \text{eV} \quad (\text{Refs. 21 and 17}),$$

$$W_a \sim 1.5 \; \text{eV} \quad (\text{Ref. 22}),$$

$$C_a \sim 1.$$

We obtain for the minimum value of δ

$$\delta_m \sim 0.01\text{-}0.04,$$

and for $2\Delta N_3$ (that is, the range of variation of electron concentration in which the C structure is stable)

$$2\Delta N_3 \sim 0.1\text{-}0.5 \; \text{electrons/atom}.$$

III. DISCUSSION

We have shown that when the electron-to-atom ratio becomes sufficiently greater than that of pure Cr, the

q vector no longer "follows the Fermi surface"; instead it changes abruptly to $\frac{1}{2}G$ and remains at that value until the electron-to-atom ratio exceeds some critical value. The physical explanation of this behavior may be understood from a consideration of the $q = \frac{1}{2}G$ state. For relatively small values of the excess e/a ratio the $q = \frac{1}{2}G$ state cannot be stable since the separation energy $E_s(\epsilon_a = 0)$ of the antiferromagnetic system would be greater than the Fermi energy of electrons in the reservoir and a transfer of electrons would take place with the resultant stability of a $q \neq \frac{1}{2}G$ state. When e/a increases to a value (ΔN_2 in Fig. 5) such that the Fermi energy of the reservoir is greater than $E_s(\epsilon_a = 0)$ the $q = \frac{1}{2}G$ state becomes *locally* stable (see Fig. 5). For sufficiently large e/a the $q = \frac{1}{2}G$ state becomes stable relative to a SDW state with $q \neq \frac{1}{2}G$ because such a state would require placing electrons in states above the lower band [see Fig. 2(B); the band b-c would become occupied], whereas in the $q = \frac{1}{2}G$ state these electrons would be only in the lower band. This accounts for the observed sticking of q at the value $\frac{1}{2}G$ as e/a increases. The first-order transition in which q jumps to $\frac{1}{2}G$ when a critical value of e/a is exceeded is directly related to the fact that $(\partial E_s/\partial \epsilon_a) < 0$ as ϵ_a approaches zero (Fig. 4). This effect takes place because in the electronic configuration the state **k** is not only connected to the state **k**+**q** via the matrix element V_q but also to the state **k**+**q*** via a similar matrix element (Fig. 2). As $\epsilon_a \rightarrow 0$ the latter effect becomes increasingly important with the result that the lower band is displaced downwards. This leads directly to the possibility of two minima in the total-energy–versus–ϵ_a curve of Fig. 5, and the jump in q at $\Delta N = \Delta N_3$. From the numerical estimates of Sec. II we can see that the present theory predicts numbers with the right order of magnitude. In fact experiment shows[17] that $\delta_m \cong 0.03$ and that the region of sticking $2\Delta N_3$ is of the order of about half an electron per atom.[24] In view of the simplicity of the model and the uncertainty in the parameters, the agreement should be considered good.

The model also provides a basis for understanding the abrupt change in δ from a finite value to zero that occurs at a temperature T_{CO} in some of the Cr-Mn alloys. The phase transition occurs because in these alloys, for $\delta = 0$, $E_s(\epsilon_a)$ is less than the Fermi energy of the reservoir. This means that the energy of the antiferromagnetic electrons does not increase greatly with increasing T whereas this is not so for the $\delta \neq 0$ state. The free energy increases more rapidly with T for the $\delta \neq 0$ state than for the $\delta = 0$ state and there is a resulting transition to the $\delta = 0$ state at sufficiently high T. Hysteresis is also to be expected in such circumstances.

[23] C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

[24] The alloys can be studied up to about 50% Mn in Cr; it is found that the C structure is stable in the range 1–50%; for more concentrated alloys the body-centered-cubic structure becomes unstable.