Spin Density Wave in Chromium and Its Alloys

Akio Shibatani

Faculty of Engineering Science, Osaka University, Toyonaka, Japan

AND

Kazuko Motizuki* and Takeo Nagamiya*

Department of Physics, University of Arizona, Tucson, Arizona 85721

(Received 24 May 1968; revised manuscript received 27 August 1968)

Antiferromagnetic, helical, and sinusoidal spin density waves (SDW) in chromium and its alloys with Mn and V are studied on the basis of a simplified model of the known band structure of chromium. Octahedral Fermi surfaces of different sizes are assumed for the electron band and hole band, and these bands are considered to play the main role in the formation of a SDW; other bands having free Fermi surfaces are considered to supply electrons to these bands during the formation of a SDW and are called the reservoir. The exchange potential for each electron due to the SDW mixes the electron band and hole band, and produces the SDW itself, so that a self-consistency equation is set up and solved. It is found that the sinusoidal SDW gives the lowest energy. Its wave vector Q at absolute zero (as well as that of a helical SDW) is the distance between the parallel surfaces of the electron and hole octahedra, but the distance changes with the supply of electrons from the reservoir. With the rigid-band model for alloys, it is found that Q jumps at a small concentration of Mn to a higher value not equal to that for the exact antiferromagnetism, in agreement with neutron observations. The observed abrupt transition to the exact antiferromagnetism at a higher concentration is not predicted, however. The Néel temperature for a second-order transition is calculated. The value of Q at the Néel temperature increases rapidly with increasing Mn concentration and attains the value for the exact antiferromagnetism, in agreement with observations. A discussion of the magnetic moment amplitude is given.

I. INTRODUCTION

PURE chromium has a sinusoidal spin order below $T_N = 310°K$, as observed by neutron diffraction experiments.[1] Its wave vector is parallel to one of the cubic principal axes, the crystal being bcc, and has a magnitude close to $2\pi/a$ (a being the lattice constant), with some variation with temperature. The spin polarization is perpendicular to the wave vector down to 121°K but becomes parallel below this temperature. The fact that the spin order remains purely sinusoidal down to very low temperatures, as far as neutron diffraction can tell, and that the specific heat anomaly at the Néel temperature is very small,[2] suggests that the spin ordering is the formation of a spin density wave (SDW) from exchange-interacting conduction-electron spins.

Neutron diffraction experiments on binary alloys,[3]

Cr-Mn and Cr-V, and ternary alloys,[4] Cr-Mn-V, show that the addition of $3d$ electrons increases both the average magnetic moment per atom and the Néel temperature. Also, it increases the magnitude of the wave vector, Q. At a certain concentration that corresponds to a few tenths of an atomic % of Mn and at temperatures immediately below T_N the magnitude of Q jumps to the exact value $2\pi/a$. At 4.2°K, however, a smaller jump (or a smaller rapid increase) to a value less than $2\pi/a$ is observed at about the same concentration. Furthermore, for concentrations exceeding 1.5 at. % the commensurable antiferromagnetism, with $2\pi/a$, is observed. The subtraction of $3d$ electrons decreases both the average magnetic moment and T_N, and it also decreases the magnitude of Q, all monotonically.

The purpose of the present paper is to develop a theory for the SDW in chromium and its alloys on the basis of the band picture of chromium and to interpret thereby some of the interesting observations mentioned above. In order to make detailed calculations possible, the band picture will be somewhat simplified, and the rigid-band model will be assumed in discussing the alloys.

As is well known, the idea of the spin density wave

* Permanent address: Faculty of Engineering Science, Osaka University, Toyonaka, Japan.

[1] C. G. Shull and M. K. Wilkinson, Rev. Mod. Phys. 25, 100 (1953); L. M. Corliss, J. M. Hastings, and R. J. Weiss, Phys. Rev. Letters 3, 211 (1959); V. N. Bykov, V. S. Golovin, N. V. Ageev, V. A. Levdik, and S. I. Vinogradov, Dokl. Akad. Nauk SSSR 128, 1153 (1959) [English transl.: Soviet Phys.—Doklady 4, 1070 (1960)]; M. K. Wilkinson, E. O. Wollan, and W. C. Koehler, Bull. Am. Phys. Soc. 5, 456 (1960); G. E. Bacon, Acta Cryst. 14, 823 (1961); V. I. Gom'ankov, D. F. Litvin, A. A. Loshmanov, and B. G. Lyaschenko, Kristallografiya 7, 790 (1962) [English transl.: Soviet Phys.—Cryst. 7, 639 (1962)]; G. Shirane and W. J. Takei, J. Phys. Soc. Japan 17, Suppl. B-III, 35 (1962); P. J. Brown, C. Wilkinson, J. B. Forsyth, and R. Nathans, Proc. Phys. Soc. (London) 85, 1185 (1965); A. Arrott, S. A. Werner, and H. Kendrick, Phys. Rev. Letters 14, 1022 (1965); S. A. Werner, A. Arrott, and H. Kendrick, Phys. Rev. 155, 528 (1967).

[2] R. H. Beaumont, H. Chihara, and J. A. Morrison, Phil. Mag. 5, 188 (1960).

[3] Y. Hamaguchi and N. Kunitomi, J. Phys. Soc. Japan 19, 1849 (1964); S. Kōmura and N. Kunitomi, J. Phys. Soc. Japan

20, 103 (1965); Y. Hamaguchi, E. O. Wollan, and W. C. Koehler, Phys. Rev. 138, A737 (1965); H. B. Møller, A. L. Trego, and A. R. Mackintosh, Solid State Commun. 3, 137 (1965); W. C. Koehler, R. M. Moon, A. L. Trego, and A. R. Mackintosh, Phys. Rev. 151, 405 (1966); T. J. Bastow, Proc. Phys. Soc. (London) 88, 935 (1966).

[4] S. Kōmura, Y. Hamaguchi, and N. Kunitomi, Phys. Letters 24A, 299 (1967); J. Phys. Soc. Japan 23, 171 (1967).

was proposed originally by Overhauser.[5] He expected a SDW state, having Q of magnitude equal to twice the Fermi radius, to be the stable state in a free electron gas. However, a number of investigators, including Hamann and Overhauser[6] as well as Fedders and Martin,[7] both of whom took properly into account the screened Coulomb interaction for the exchange interaction among the electrons, have disproved the stability of a spin density wave in a three-dimensional free electron gas. On the other hand, a study of a specialized single-band model made by Tachiki and Nagamiya[8] and Nagamiya and co-workers,[9] as well as that made by Penn,[10] have shown that a spin density wave is stable in a certain range of the values of the parameters involved in the theory. The band models they assumed are, however, remote from the band in chromium. All these theories are based on the Hartree-Fock approximation, as will be the theory of the present paper.

The band structure of chromium has become known well in recent years by a theoretical consideration of Lomer,[11] indirect information gathered from experiments on Mo and W,[12] and band calculations made by Loucks,[13] Mattheiss[14] (for W), and Asano and Yamashita.[15] In the paramagnetic state, there is an electron Fermi surface of nearly octahedral shape at the center of the Brillouin zone, and there are hole Fermi surfaces around the $\langle 100 \rangle$ corners of the Brillouin zone, which also form an approximate octahedron in the repeated zone scheme. Furthermore, there are six smaller electron Fermi surfaces located between the central electron Fermi surface and the hole Fermi surfaces at the corners, and it was shown[15] that a high density of states is associated with these six Fermi surfaces.[16] It was sug-

gested by Lomer[11] that the central electron Fermi surface and the corner hole Fermi surfaces would be responsible for stabilizing a SDW. A SDW having Q that measures the distance between one side of the electron octahedron and the same side of the hole octahedron will couple the Bloch states of the electron band to the Bloch states of the hole band in such a way that the occupied states in both bands are lowered and the unoccupied states are elevated. A self-consistent treatment based on this idea was made by Fedders and Martin[7] in a simplified way, and they obtained good results for the relation between T_N and the amplitude of the SDW at absolute zero, as well as for the variation of the amplitude with temperature. However, they assumed spheres of the same size for the electron and hole surfaces and disregarded the periodicity of the energy surfaces in the reciprocal-lattice space, so that they could not give any information about the value of Q nor could discuss the relative stability of a helical SDW and a sinusoidal SDW.

In the present paper we replace the near octahedra of the electron and hole Fermi surfaces by exact octahedrons, a smaller octahedron being assumed for the electron Fermi surface than for the hole Fermi surface in the case of the pure chromium. In the case of alloys the sizes of these octahedra are varied in accordance with the number of $3d$ electrons, using rigid-band model. We discuss the relative stability of three SDW's: helical and sinusoidal SDW's with Q not equal to $2\pi/a$ and exact antiferromagnetic SDW with $Q = 2\pi/a$. We also consider a flow of electrons from the third band (having six Fermi surfaces at intermediate positions) to the electron and hole bands that participate in the formation of the SDW. This flow, which occurs in the process of the formation of the SDW, is found to be important. Finally, we study the Néel temperature and the value of Q at the Néel temperature.

[5] A. W. Overhauser, Phys. Rev. Letters **4**, 462 (1960); J. Phys. Chem. Solids **13**, 71 (1960); Phys. Rev. **128**, 1437 (1962).
[6] D. R. Hamann and A. W. Overhauser, Phys. Rev. **143**, 183 (1966).
[7] P. A. Fedders and P. C. Martin, Phys. Rev. **143**, 245 (1966).
[8] M. Tachiki and T. Nagamiya, Phys. Letters **3**, 214 (1963).
[9] T. Nagamiya, K. Motizuki, and K. Yamasaki, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 195; R. Mitsudo, K. Motizuki, and T. Nagamiya, J. Phys. Soc. Japan **20**, 710 (1965).
[10] D. R. Penn, Phys. Rev. **142**, 350 (1966).
[11] W. M. Lomer, Proc. Phys. Soc. (London) **80**, 489 (1962); **84**, 327 (1964); in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 127.
[12] E. Fawcett and W. M. Walsh, Jr., Phys. Rev. Letters **8**, 476 (1962); E. Fawcett and D. Griffiths, J. Phys. Chem. Solids **23**, 1631 (1962); G. B. Brandt and J. A. Rayne, Phys. Rev. **132**, 1945 (1963); J. A. Rayne, *ibid.* **133**, A1104 (1964); C. K. Jones and J. A. Rayne, Phys. Letters **8**, 155 (1964).
[13] T. L. Loucks, Phys. Rev. **139**, A1181 (1965).
[14] L. F. Mattheiss, Phys. Rev. **139**, A1893 (1965).
[15] S. Asano and J. Yamashita, J. Phys. Soc. Japan **23**, 714 (1967).
[16] There are also hole Fermi surfaces centered at each face center of the Brillouin zone dodecahedron. These are reported to be associated mainly with p-type wave functions. We neglect them or we may include them in what we call the reservoir. Other Fermi surfaces reported are associated mainly with d-type wave functions.

II. GENERAL IDEA OF THE THEORY

To avoid complications that we would meet in the exact Hartree-Fock treatment, we adopt in our line of thought an approximation introduced by Slater[17] where the exchange effect is taken care of by an exchange potential common to all electrons. If, further, the electron system is approximated at each local point by an ensemble of free electrons, then this exchange potential is given by $-3e^2(3/4\pi)^{1/3}(n_\pm)^{1/3}$, where $n_\pm$ are the number densities of up-spin electrons and down-spin electrons, respectively, at a point under consideration. [An electron with up or down spin digs a hole of radius $r_\pm = (4\pi n_\pm/3)^{-1/3}$ in the sea of up- or down-spin electrons by the Pauli principle, and this hole gives an electrostatic potential energy for the electron which is approximately equal to $-3e^2(3/4\pi)^{1/3}(n_\pm)^{1/3}$.] If we denote by $V_\pm(\mathbf{r})$ the exchange potentials for up-spin

[17] J. C. Slater, Phys. Rev. **81**, 385 (1951).

electrons and down-spin electrons, respectively, and write $\frac{1}{2}[V_+(\mathbf{r})-V_-(\mathbf{r})]=V(\mathbf{r})$, then an up-spin electron is subject to the potential $V(\mathbf{r})$ and a down-spin electron to $-V(\mathbf{r})$, besides to the common exchange potential $\frac{1}{2}[V_+(\mathbf{r})+V_-(\mathbf{r})]$ and the Coulomb potential.

When there is a SDW, the net spin density, $\mathbf{S}(\mathbf{r})$, is a function of position $\mathbf{r}$; both its magnitude and its direction vary with $\mathbf{r}$. If the direction of $\mathbf{S}(\mathbf{r})$ at point $\mathbf{r}$ is denoted by ζ, the potentials $V(\mathbf{r})$ and $-V(\mathbf{r})$ may be written collectively as $V(\mathbf{r})\sigma_\zeta$, where σ_ζ is the Pauli spin matrix. If we denote by x, y, z the coordinate system fixed in space and by l, m, n the direction cosines of ζ, then we can write $\sigma_\zeta=l\sigma_x+m\sigma_y+n\sigma_z$. Writing $V(\mathbf{r})l=V_x(\mathbf{r})$, $V(\mathbf{r})m=V_y(\mathbf{r})$, $V(\mathbf{r})n=V_z(\mathbf{r})$, we have

$$V(\mathbf{r})\sigma_\zeta=V_x(\mathbf{r})\sigma_x+V_y(\mathbf{r})\sigma_y+V_z(\mathbf{r})\sigma_z=\mathbf{V}(\mathbf{r})\cdot\boldsymbol{\sigma}.$$

Thus, each electron is subject to the spin-dependent potential $\mathbf{V}(\mathbf{r})\cdot\boldsymbol{\sigma}$ besides the spin-independent Coulomb and exchange potentials. If there is no variation of electron density in association with the SDW, the Coulomb potential is a periodic function of the lattice. Still, the spin-independent exchange potential, $\frac{1}{2}[V_+(\mathbf{r})+V_-(\mathbf{r})]$, may vary with the period of the SDW, since $n_+^{1/3}$ and $n_-^{1/3}$ cannot be identified with $[(n_++n_-)/2]^{1/3}$ unless the difference between n_+ and n_- is small. We shall, however, assume that n_+-n_- is small (compared with n_++n_-) so that the spin-independent potentials are functions with the lattice period only and they determine the Bloch functions. In this approximation we obtain the proportionality between $\mathbf{V}(\mathbf{r})$ and $\mathbf{S}(\mathbf{r})$, i.e., $\mathbf{V}(\mathbf{r})=-J\mathbf{S}(\mathbf{r})$, where J is, in general, a periodic function of the lattice but we assume it to be a constant. (For our discussions in subsequent sections it does not matter whether J is a constant or a periodic function of the lattice.)

The self-consistent treatment of a SDW will be as follows. We take linear combinations of Bloch functions with up and down spins to diagonalize $\mathbf{V}(\mathbf{r})\cdot\boldsymbol{\sigma}$. The corresponding eigenfunctions will be denoted by $\psi_{i\mathbf{k}}$, i being the index of the new bands and $\mathbf{k}$ the wave vector of the representative Bloch function contained in the eigenfunction. The spin density $\mathbf{S}(\mathbf{r})$ is then obtained as $\sum_i\sum_{\mathbf{k}}\psi_{i\mathbf{k}}{}^*\cdot(\boldsymbol{\sigma}/2)\psi_{i\mathbf{k}}$, where the double summation is extended over occupied eigenstates and the center dot means summation over spin variable. While this is the spin density at absolute zero, the spin density at a finite temperature can be obtained by putting the Fermi distribution factor to the summand and taking summation over all possible states. The spin density thus obtained, times $-J$, must be equal to $\mathbf{V}(\mathbf{r})$, and this equation is the self-consistency condition.

Instead of solving the self-consistency equation directly, we may take the matrix elements of both sides of it with respect to Bloch functions and solve the resulting equations, since Bloch functions form a complete set. This procedure will be followed in the

present paper. However, we shall take the average of the matrix elements over the Bloch states and hence deal with a single self-consistency equation, instead of a system of equations.

In the present paper we study three types of SDW, i.e., antiferromagnetic, helical, and sinusoidal SDW's, and compare their relative stability by calculating their total energies. We consider that the bands associated with the Fermi surfaces of electron and hole octahedra play the essential role in the formation of a SDW and assume that the wave vector $\mathbf{Q}$ for the helical and sinusoidal SDW's is such that it measures the distance between the parallel surfaces of the electron octahedron and hole octahedron, as long as we are concerned with absolute zero. This gives the lowest energy, and in fact we checked it by some numerical computations. However, we do not merely take the Fermi surfaces that we have in the paramagnetic state. We consider a possible flow of electrons from the third band (which we shall refer to as *reservoir*) to the bands of electron and hole octahedra. By this flow the electron octahedron will enlarge and the hole octahedron will diminish, if no SDW is yet formed. We take the value of Q to be the distance between the parallel surfaces of these new Fermi surfaces, but we determine the amount of flow and hence the value of Q by minimizing the total energy of the system after constructing the SDW. The total energy will consist of two: the work necessary to transfer an amount of electrons from the reservoir to the bands of electron and hole octahedra, and the formation energy of the SDW. The latter is calculated by taking the sum of the one-electron energy eigenvalues of the occupied states in the presence of the SDW and subtracting half the sum of the one-electron exchange potential energies.

The Néel temperature is determined as the temperature where the amplitude of the SDW vanishes, provided we assume a transition of the second order. In the present paper we shall not calculate the temperature dependence of the SDW amplitude. We shall calculate only the Néel temperature, assuming a transition of the second order. Here the value of Q is not necessarily the same as that for absolute zero. We have to determine it by minimizing the free energy of the system; alternatively, we may determine it by maximizing the Néel temperature with respect to Q. Our calculation will show that the value of Q thus determined is different from that for absolute zero.

Furthermore, the Fermi level will, in general, vary slightly with temperature, and this will affect the Néel temperature and Q. We shall give some discussion on this point in Sec. VII.

III. ANTIFERROMAGNETIC SDW

In this section and in Secs. IV and V we shall disregard the electron flow from the reservoir to the electron and hole bands participating in the formation of a

SDW. By band a we denote the band having the octahedral electron Fermi surface at the center of the Brillouin zone, and by band b, the band having the octahedral hole Fermi surface at $\langle 100 \rangle$ corners of the Brillouin zone. Matrix elements of the SDW exchange potential between bands a and b will be considered, but matrix elements within the same band and those involving the reservoir will be neglected. The octahedral form of the Fermi surfaces of bands a and b will be assumed as exact, and writing the component of $\sqrt{3}\mathbf{k}$ normal to the octahedral surface in each octant (i.e., $k_x+k_y+k_z$ in the first octant) simply by k, we assume the following linear energy spectrum for band a:

$$\epsilon_a(\mathbf{k}) = \alpha(k-k_e), \tag{1}$$

where k_e is the value of k at the Fermi surface. Similarly, for band b we assume

$$\epsilon_b(\mathbf{k}) = -\beta(k-k_h), \tag{2}$$

where k is again the normal component of $\sqrt{3}$ times the wave vector measured from the center of the hole octahedron (Fig. 1). Considering band calculations, we assume for pure chromium $k_e=0.35$ and $k_h=0.40$ in units of $2\pi/a$; these values are somewhat smaller than those obtainable from Ref. 15. We write $k_h-k_e=\delta_0$, reserving δ without suffix for the value of k_h-k_e that we would have when we force a flow from the reservoir in the paramagnetic state. δ_0 depends on the concentration of $3d$ electrons when we consider alloys.

We first consider antiferromagnetic SDW with $Q=2\pi/a$ at absolute zero. For convenience, the spin polarization will be assumed to be along the x axis. Then the exchange potential of the SDW will take the
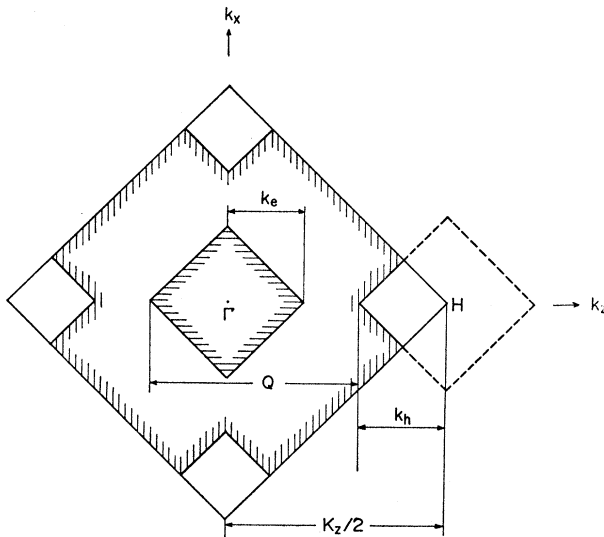

FIG. 1. Schematic representation of the electron Fermi surface of size k_e and the hole Fermi surface of size k_h in the Brillouin zone. Q is the magnitude of the wave vector of the helical or sinusoidal SDW at absolute zero.
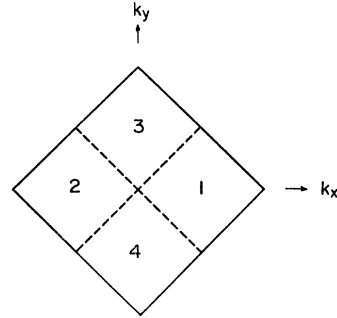

FIG. 2. Partition of the Brillouin zone into six octahedral domains in the case of an antiferromagnetic SDW; the (k_z,k_y) cross section is shown.

form

$$V(\mathbf{r})\sigma_x = \tfrac{1}{3}U(\mathbf{r})[\cos(\tfrac{1}{2}\mathbf{K}_x\cdot\mathbf{r})+\cos(\tfrac{1}{2}\mathbf{K}_y\cdot\mathbf{r}) \\ +\cos(\tfrac{1}{2}\mathbf{K}_z\cdot\mathbf{r})]\sigma_x, \tag{3}$$

where $U(\mathbf{r})$ is a function having the bcc space group symmetry with maxima at atomic positions and $\mathbf{K}_x=(4\pi/a,0,0)$, etc., are reciprocal lattice vectors parallel to the cubic principal axes; the sum of cosines in (3) represents the antiferromagnetic pattern, taking a value of 3 at corner sites and a value of -3 at body-center sites. Writing the Bloch functions of bands a and b as

$$\phi_{a\mathbf{k}} = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}), \quad \phi_{b\mathbf{k}} = \exp(i\mathbf{k}\cdot\mathbf{r})v_{\mathbf{k}}(\mathbf{r}), \tag{4}$$

we take the matrix element of the potential (3) with respect to $\phi_{a\mathbf{k}}\alpha$ and $\phi_{b\mathbf{k}'}\beta$, α and β being up- and down-spin functions. This matrix element is nonvanishing only when $\mathbf{k}'\equiv\mathbf{k}+\mathbf{K}_i/2$ $(i=x,y,z)$, where $\equiv$ means equivalency, or equality up to an additive reciprocal lattice vector. The same matrix element exists between $\phi_{a\mathbf{k}}\beta$ and $\phi_{b\mathbf{k}'}\alpha$. We write

$$V_{\mathbf{k}\mathbf{k}'} = \int \phi_{a\mathbf{k}}{}^*V(\mathbf{r})\phi_{b\mathbf{k}'}d\mathbf{r}$$

$$= \int V(\mathbf{r})\exp(\pm\tfrac{1}{2}i\mathbf{K}_i\cdot\mathbf{r})u_{\mathbf{k}}{}^*(\mathbf{r})v_{\mathbf{k}'}(\mathbf{r})d\mathbf{r}. \tag{5}$$

Here we take $\pm\mathbf{K}_i$ as follows. We divide the Brillouin zone by (110)-type planes into six octahedral domains, 1, 2, $\cdots$, 6, as shown in Fig. 2. If $\mathbf{k}$ is in domain 1, then $\mathbf{k}'=\mathbf{k}-\mathbf{K}_x/2$ is in domain 2, so that we take $-\mathbf{K}_x$ for $\pm\mathbf{K}_i$; if k is in domain 2, then $\mathbf{k}'=\mathbf{k}+\tfrac{1}{2}\mathbf{K}_x$ is in domain 1, so that we take $+\mathbf{K}_x$, and so on.

Corresponding to nonvanishing $V_{\mathbf{k}\mathbf{k}'}$ given by Eq. (5), we obtain energy eigenvalues from

$$\begin{vmatrix} \epsilon_a(\mathbf{k})-E & V_{\mathbf{k}\mathbf{k}'} \\ V_{\mathbf{k}\mathbf{k}'}{}^* & \epsilon_b(\mathbf{k}')-E \end{vmatrix} = 0$$

as

$$E=E_{\mathbf{k}}{}^{\pm}=\tfrac{1}{2}[\epsilon_a(\mathbf{k})+\epsilon_b(\mathbf{k}')] \\ \pm\{\tfrac{1}{4}[\epsilon_a(\mathbf{k})-\epsilon_b(\mathbf{k}')]^2+|V_{\mathbf{k}\mathbf{k}'}|^2\}^{1/2} \tag{6}$$

and eigenfunctions as

$$\psi_k = A_k \phi_{ak}\alpha + B_{k'}\phi_{bk'}\beta, \quad \psi_{k'} = A_k \phi_{ak}\beta + B_{k'}\phi_{bk'}\alpha, \quad (7)$$

where

$$A_k = V_{kk'}/\{[\epsilon_a(k)-E]^2 + |V_{kk'}|^2\}^{1/2}, \quad (8a)$$

$$B_{k'} = -[\epsilon_a(k)-E]/\{[\epsilon_a(k)-E]^2 + |V_{kk'}|^2\}^{1/2}. \quad (8b)$$

From Eqs. (6), (8a), and (8b) it follows that

$$A_k B_{k'} = \pm \tfrac{1}{2} V_{kk'}/\{\tfrac{1}{4}[\epsilon_a(k)-\epsilon_b(k')]^2 + |V_{kk'}|^2\}^{1/2}. \quad (9)$$

The spin density $S(r)$ can be calculated as the following sum over occupied eigenstates:

$$S(r) = \sum_{occ.} [\psi_k^* \cdot (\tfrac{1}{2}\sigma_x)\psi_k + \psi_{k'}^* \cdot (\tfrac{1}{2}\sigma_x)\psi_{k'}]$$

$$= \sum_{occ.} [A_k^* B_{k'}\phi_{ak}^*\phi_{bk'} + A_k B_{k'}^*\phi_{ak}\phi_{bk'}^*]$$

$$= \sum_{occ.} [A_k^* B_{k'} \exp(\pm\tfrac{1}{2}iK_i\cdot r)u_k^* v_{k'}$$

$$+\text{complex conjugate}]. \quad (10a)$$

This function has the antiferromagnetic pattern, since by displacement $r \rightarrow r + (\tfrac{1}{2}a,\tfrac{1}{2}a,\tfrac{1}{2}a)$ the exponential factor in (10a) changes sign, u_k^* and $v_{k'}$ do not change, and obviously the function has cubic symmetry. The two conjugate terms in (10a) are equal to each other when summed over occupied states. To see that, we choose for convenience the phase factors of the Bloch functions in such a way that $u_{-k} = u_k^*$, $v_{-k} = v_k^*$. Then $V_{-k,-k'} = V_{kk'}^*$, so that $A_{-k}^* B_{-k'} = A_k B_{k'}^* = A_k B_{k'}$ ($B_{k'}$ is real). In the sum of the first term of (10a) we replace k and k' by $-k$ and $-k'$, respectively. Then we obtain the sum of the second term. Thus,

$$S(r) = \sum_{occ.} 2[A_k B_{k'} \exp(\mp\tfrac{1}{2}iK_i\cdot r)u_k v_{k'}^*]. \quad (10b)$$

The self-consistency equation is $V(r) = -JS(r)$. Instead of dealing with it directly, we multiply both sides of it by $\phi_{ak}^* \phi_{bk'}$ ($\kappa' = \kappa \pm \tfrac{1}{2}K_j$, $j=x, y, z$) and integrate. Then we have

$$V_{\kappa\kappa'} = -2J \sum_{occ.} A_k B_{k'} \int \exp[\tfrac{1}{2}i(\mp K_i \pm K_j)\cdot r]$$

$$\times u_k v_{k'}^* u_\kappa^* v_{\kappa'} dr. \quad (11)$$

(Here J could be placed after the integration symbol if it is a periodic function of r.) We now make the approximation of replacing the integral of Eq. (11) by a positive constant γ^2 and $V_{kk'}$ (also $V_{\kappa\kappa'}$) by a positive constant g. The nature of this approximation will be discussed later. Then, using Eq. (9), Eq. (11) can be written in a simple form as follows:

$$g = J\gamma^2 g \sum_{occ.} \mp\{\tfrac{1}{4}[\epsilon_a(k)-\epsilon_b(k')]^2 + g^2\}^{-1/2}. \quad (12)$$

This is the self-consistency equation to determine g, or the gap $2g$ which appears in the energy expression

(6) for $\epsilon_a(k) = \epsilon_b(k')$. The double sign in Eq. (12) corresponds to that in Eq. (6). The solution $g=0$ gives the paramagnetic state, whereas the nonzero solution gives the state of a SDW. The latter was computed numerically, and the results will be presented in Sec. VIII. For finite temperatures we have the Fermi distribution factor $f(E_k^\pm) = [\exp(E_k^\pm - E_F)/kT + 1]^{-1}$ in the right-hand side of Eq. (12).

In order to see whether or not the SDW state is more stable than the paramagnetic state, we calculate the total energy of the system in the SDW state referred to that in the paramagnetic state. This energy is expressed as

$$E_{SDW} = \sum_{occ.} \{2E_k^\pm - \tfrac{1}{2}[\langle\psi_k^*| V(r)\sigma_x |\psi_k\rangle$$

$$+ \langle\psi_{k'}^*| V(r)\sigma_x |\psi_{k'}\rangle]\}$$

$$- \sum_{occ.} 2[\epsilon_a(k)+\epsilon_b(k)]. \quad (13)$$

The first summation is extended over occupied eigenstates in the presence of the SDW and the second summation over occupied states in the paramagnetic state. The factor 2 to $E_k^\pm$ cares for the two eigenfunctions ψ_k and $\psi_{k'}$ which have the same energy eigenvalue, and the factor 2 in the paramagnetic term is for the spin degeneracy. With the use of Eqs. (6) and (7), and with the approximation made above, E_{SDW} can be written as follows:

$$E_{SDW} = 2 \sum_{occ.} \mp[|x| - (x^2 + g^2)^{1/2}$$

$$+ \tfrac{1}{2}g^2(x^2+g^2)^{-1/2}], \quad (14)$$

$$x = \tfrac{1}{2}[\epsilon_a(k) - \epsilon_b(k')]. \quad (15)$$

Numerical results for E_{SDW} will be discussed also in Sec. VIII.

In the rest of this section we discuss the validity of the approximation of replacing the integral of Eq. (11) by γ^2 and $V_{kk'}$ by g. This is made in two steps. We first assume that $u_k(r)$ and $v_k(r)$ are well localized around atomic positions. This assumption is supported by band calculations.[15] We express Bloch functions in terms of Wannier functions:

$$\phi_{ak}(r) = N^{-1/2} \sum_n \exp(ik\cdot R_n)w_a(r-R_n),$$

$$\phi_{bk}(r) = N^{-1/2} \sum_n \exp(ik\cdot R_n)w_b(r-R_n),$$

where R_n's are the atomic positions and N is the total number of atoms. Then,

$$V_{kk'} = N^{-1} \sum_m \sum_n \exp(-ik\cdot R_m + ik'\cdot R_n)$$

$$\times \int V(r)w_a^*(r-R_m)w_b(r-R_n)dr.$$

The Wannier functions are well localized, so that the integral has an appreciable value only when $\mathbf{R}_m = \mathbf{R}_n$. Hence, for $\mathbf{k}' = \mathbf{k} \pm \frac{1}{2}\mathbf{K}_i$,

$$V_{\mathbf{k}\mathbf{k}'} = N^{-1} \sum_n \exp(\pm \frac{1}{2}i\mathbf{K}_i \cdot \mathbf{R}_n)$$

$$\times \int V(\mathbf{r})w_a{}^*(\mathbf{r}-\mathbf{R}_n)w_b(\mathbf{r}-\mathbf{R}_n)d\mathbf{r}.$$

The exponential factor in this expression is 1 for corner sites and -1 for body-center sites, and $V(\mathbf{r})$ has opposite signs at these sites according to Eq. (3). Therefore we can write

$$V_{\mathbf{k}\mathbf{k}'} = \int V(\mathbf{r})w_a{}^*(\mathbf{r})w_b(\mathbf{r})d\mathbf{r},$$

which is a constant independent of $\mathbf{k}$, $\mathbf{k}'$. The integral appearing in Eq. (11) can be treated in a similar way. The vector $\frac{1}{2}(\mp \mathbf{K}_i \pm \mathbf{K}_j)$ is a reciprocal lattice vector, so that $\exp[\frac{1}{2}i(\mp \mathbf{K}_i \pm \mathbf{K}_j) \cdot \mathbf{R}_n] = 1$. Hence the integral can be written as

$$N^{-1} \int |w_a(\mathbf{r})|^2 |w_b(\mathbf{r})|^2 d\mathbf{r} = \gamma^2,$$

which is a positive constant.

In the second step we consider a more general case. Since the bands a and b have cubic symmetry in $\mathbf{k}$ space, their Bloch functions can be assumed as invariant under simultaneous cubic rotations of the $\mathbf{r}$ space and $\mathbf{k}$ space. Furthermore, they are invariant under simultaneous inversion of the two spaces. The inversion gives the relations

$$\begin{aligned} u_{-\mathbf{k}}(-\mathbf{r}) &= u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}{}^*(-\mathbf{r}), \\ v_{-\mathbf{k}}(-\mathbf{r}) &= v_{\mathbf{k}}(\mathbf{r}) = v_{\mathbf{k}}{}^*(-\mathbf{r}). \end{aligned} \tag{16}$$

By replacing the integration variable $\mathbf{r}$ in (5) by $-\mathbf{r}$, we see that $V_{\mathbf{k}\mathbf{k}'}$ is equal to its complex conjugate, i.e., it is real. This will support the replacement of $V_{\mathbf{k}\mathbf{k}'}$ by a real constant g, if we take its average over $\mathbf{k}$. Although the averaging procedure cannot be defined precisely, we may consider that $V_{\mathbf{k}\mathbf{k}'}$ has cubic symmetry in $\mathbf{k}$ space and that the most important contribution of $V_{\mathbf{k}\mathbf{k}'}$ to the self-consistency equation arises from those $\mathbf{k}$ which are in the vicinity of the Fermi surface of band a and for which the corresponding $\mathbf{k}'$ are in the vicinity of the Fermi surface of band b. Thus, taking an average of $V_{\mathbf{k}\mathbf{k}'}$ with some weight near the Fermi surfaces, we may be allowed to replace $V_{\mathbf{k}\mathbf{k}'}$ by its average value.

Since $A_{\mathbf{k}}B_{\mathbf{k}'}$ also has cubic symmetry, we may replace the integral in Eq. (11) by its average over $\mathbf{k}$. Further, we take the average of the result over $\varkappa$.

Then we have

$$\gamma^2 = \int |\langle \exp(\mp \frac{1}{2}i\mathbf{K}_i \cdot \mathbf{r})u_{\mathbf{k}}v_{\mathbf{k}'}{}^*\rangle|^2 d\mathbf{r}. \tag{17}$$

This is a positive real constant.

IV. HELICAL SDW

If we suppose that the antiferromagnetic SDW pattern whose exchange potential is represented by Eq. (3) is twisted about the z axis with a wave vector of magnitude $q(=2\pi/a-Q)$, then we would have an exchange potential of the form

$$V(\mathbf{r})(\sigma_x \cos qz + \sigma_y \sin qz), \tag{18}$$

where $V(\mathbf{r})$ has the antiferromagnetic pattern represented by Eq. (3). Generally, however, the spin direction may not turn uniformly as the position advances in the z direction, that is, it may stay nearly constant in the neighborhood of the $3d$ shell of an atom, turn swiftly between atoms, and then stay again nearly constant in the neighborhood of the $3d$ shell of the adjacent atom. Therefore, the general form of the exchange potential will be of the form

$$V(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r})s^+ + V(\mathbf{r})^* \exp(i\mathbf{q} \cdot \mathbf{r})s^-, \tag{19}$$

where

$$s^+ = \frac{1}{2}(\sigma_x + i\sigma_y), \quad s^- = \frac{1}{2}(\sigma_x - i\sigma_y),$$

and where $V(\mathbf{r})$ is now a complex function whose phase angle varies with the period of the lattice in such a way that it changes by π in going from a corner site to a neighboring body-center site. The sum of the phase angle of $V(\mathbf{r})^*$ and the angle $\mathbf{q} \cdot \mathbf{r}$ is the angle specifying the direction of the spin density vector in the xy plane. Taking the origin of $\mathbf{r}$ at an atomic site, we assume for convenience that the phase angle of $V(\mathbf{r})^*$ is zero at $\mathbf{r}=0$.

Furthermore, we may assume that the spin density pattern has inversion symmetry with respect to $\mathbf{r}=0$, i.e., that we see the same rotation and the same variation of the spin density vector when we go from the origin in any opposite directions. This means that we may assume $V(-\mathbf{r}) = V(\mathbf{r})^*$. We will show later that with this assumption we obtain a spin density pattern having the inversion symmetry so that the assumption is self-consistently supported. Other symmetry property of $V(\mathbf{r})$ is its tetragonality, since we assume $\mathbf{q}$ to be parallel to the z axis, i.e., the [001] axis.

The first term of (19) has a nonvanishing matrix element between $\phi_{a\mathbf{k}}{}^*\alpha$ and $\phi_{b\mathbf{k}'}\beta$ for $\mathbf{k}' = \mathbf{k} + \mathbf{q} \pm \frac{1}{2}\mathbf{K}_i$. This matrix element can be written in the same form as (5). In the present case, we divide the Brillouin zone into six domains by (110)-type planes in the way shown in Figs. 3(a) and 3(b); these planes meet at the point $\mathbf{k} = -\mathbf{q}$ and the point $\mathbf{k} = \mathbf{q}$, respectively. If $\mathbf{k}$ is in domain 1 of Fig. 3(a), then $\mathbf{k}' = \mathbf{k} + \mathbf{q} - \frac{1}{2}\mathbf{K}_x$ is in
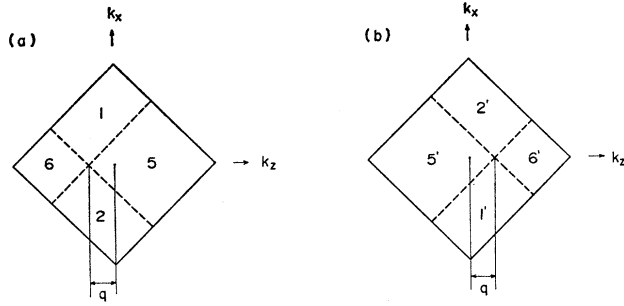
FIG. 3. Partition of the Brillouin zone into six domains in the case of a helical SDW; (a): domains for $\mathbf{k}$, (b): domains for $\mathbf{k}'=\mathbf{k}+\mathbf{q}+\frac{1}{2}\mathbf{K}_i$, $i=x,y,z$; $\mathbf{q}=\frac{1}{2}\mathbf{K}_z-\mathbf{Q}$.

domain $1'$ of Fig. 3(b); if $\mathbf{k}$ is in domain 2, then $\mathbf{k}'=\mathbf{k}+\mathbf{q}+\frac{1}{2}\mathbf{K}_x$ is in domain $2'$, and so on. The second term of (19) has a nonvanishing matrix element between $\phi_{a\mathbf{k}}{}^*\beta$ and $\phi_{b\mathbf{k}'}\alpha$ for $\mathbf{k}'\equiv\mathbf{k}-\mathbf{q}\pm\frac{1}{2}\mathbf{K}_i$. The domains for $\mathbf{k}$ and those for $\mathbf{k}'$ are interchanged. The matrix element is the same as (5), except that $V(\mathbf{r})$ is replaced by $V(\mathbf{r})^*$. Replacing the integration variable $\mathbf{r}$ by $-\mathbf{r}$ and using the relations (16) (the first equality), we see that the matrix element is $V_{-\mathbf{k},-\mathbf{k}'}$. Furthermore, replacing $\mathbf{r}$ by $-\mathbf{r}$ in (5) and using the second equality of (16), we see that $V_{\mathbf{k}\mathbf{k}'}=V_{\mathbf{k}\mathbf{k}'}{}^*$. The eigenfunctions are, therefore, expressed in the forms

$$\psi_{\mathbf{k}}=A_{\mathbf{k}}\phi_{a\mathbf{k}}\alpha+B_{\mathbf{k}'}\phi_{b\mathbf{k}'}\beta \quad (\mathbf{k}'=\mathbf{k}+\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_i), \quad (20)$$

$$\psi_{\mathbf{k}'}=A_{-\mathbf{k}}\phi_{a\mathbf{k}}\beta+B_{-\mathbf{k}'}\phi_{b\mathbf{k}'}\alpha \quad (\mathbf{k}'=\mathbf{k}-\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_i), \quad (21)$$

where $A_{\mathbf{k}}$ and $B_{\mathbf{k}'}$ are given by (8a) and (8b), respectively, and are real.

The spin density can be calculated as follows. For the minus component we have

$$S^-(\mathbf{r})=\sum_{\mathrm{occ.}}[\psi_{\mathbf{k}}{}^*\cdot s^-\psi_{\mathbf{k}}+\psi_{\mathbf{k}'}{}'^*\cdot s^-\psi_{\mathbf{k}}{}']$$

$$=\sum_{\mathrm{occ.}} A_{\mathbf{k}}B_{\mathbf{k}'}u_{\mathbf{k}}v_{\mathbf{k}'}{}^*\exp(\mp\tfrac{1}{2}i\mathbf{K}_i\cdot\mathbf{r})\exp(-i\mathbf{q}\cdot\mathbf{r})$$

$$+\sum_{\mathrm{occ.}} A_{-\mathbf{k}}B_{-\mathbf{k}'}u_{\mathbf{k}}{}^*v_{\mathbf{k}'}\exp(\pm\tfrac{1}{2}i\mathbf{K}_i\cdot\mathbf{r})\exp(-i\mathbf{q}\cdot\mathbf{r}),$$

where in the first sum over occupied eigenstates $\mathbf{k}'$ is $\mathbf{k}+\mathbf{q}\pm\frac{1}{2}\mathbf{K}_i$ and in the second sum over occupied states $\mathbf{k}'$ is $\mathbf{k}-\mathbf{q}\pm\frac{1}{2}\mathbf{K}_i$. Replacing $\mathbf{k}$ and $\mathbf{k}'$ by $-\mathbf{k}$ and $-\mathbf{k}'$ in the second sum, we see that this sum is equal to the first sum. Thus,

$$S^-(\mathbf{r})=2\sum_{\mathrm{occ.}} A_{\mathbf{k}}B_{\mathbf{k}'}u_{\mathbf{k}}v_{\mathbf{k}'}{}^*\exp(\mp\tfrac{1}{2}i\mathbf{K}_i\cdot\mathbf{r})$$

$$\times\exp(-i\mathbf{q}\cdot\mathbf{r}),$$

$$(\mathbf{k}'=\mathbf{k}+\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_i). \quad (22)$$

The complex conjugate of this expression is obtained for $S^+(\mathbf{r})$. The exchange potential (19) should be equal to $-J[S^-(\mathbf{r})s^++S^+(\mathbf{r})s^-]$, so that the self-consistency

equation is

$$V(\mathbf{r})=-2J\sum_{\mathrm{occ.}} A_{\mathbf{k}}B_{\mathbf{k}'}u_{\mathbf{k}}(\mathbf{r})v_{\mathbf{k}'}{}^*(\mathbf{r})\exp(\mp\tfrac{1}{2}i\mathbf{K}_i\cdot\mathbf{r}). \quad (23)$$

Here the coefficient $A_{\mathbf{k}}B_{\mathbf{k}'}$ is given by Eq. (9). We see from Eq. (23) that, by inversion, $V(\mathbf{r})$ changes to its complex conjugate. Furthermore, $V(\mathbf{r})$ is clearly a periodic function changing sign by displacement $\mathbf{r}\to\mathbf{r}+(\frac{1}{2}a,\frac{1}{2}a,\frac{1}{2}a)$. Since $\mathbf{q}$ is assumed to be parallel to [001], $\mathbf{k}$ and $\mathbf{k}'$ of the occupied eigenstates have tetragonal symmetry in $\mathbf{k}$ space, so that $V(\mathbf{r})$ also has tetragonal symmetry in $\mathbf{r}$ space.

We multiply both sides of Eq. (23) by $\phi_{a\kappa}{}^*\phi_{b\kappa'}$ $\times\exp(-i\mathbf{q}\cdot\mathbf{r})$, where $\kappa'=\kappa+\mathbf{q}\pm\frac{1}{2}\mathbf{K}_j$, and integrate. Then we have

$$V_{\kappa\kappa'}=-2J\sum_{\mathrm{occ.}} A_{\mathbf{k}}B_{\mathbf{k}'}\int\exp[\tfrac{1}{2}i(\mp\mathbf{K}_i\pm\mathbf{K}_j)\cdot\mathbf{r}]$$

$$\times u_{\mathbf{k}}v_{\mathbf{k}'}{}^*u_{\kappa}{}^*v_{\kappa'}d\mathbf{r}. \quad (24)$$

As in Sec. III, we replace $V_{\mathbf{k}\mathbf{k}'}$ and $V_{\kappa\kappa'}$ by a constant g [$V_{\mathbf{k}\mathbf{k}'}$ appears in Eq. (9) for $A_{\mathbf{k}}B_{\mathbf{k}'}$] and the integral of Eq. (24) by a positive constant γ^2 after replacing it by its average over $\mathbf{k}$ and κ, as expressed by Eq. (17). The value of γ^2 for the present case can be different from that for the exact antiferromagnetic case, since $\mathbf{k}$ and $\mathbf{k}'$ are not related in the same way. However, if one replaces $\mathbf{q}$ by $-\mathbf{q}$, the value of γ^2 in the present case, defined by Eq. (17), goes over to itself. To see that, consider first that $\mathbf{k}$ and $\mathbf{k}'$ are related by $\mathbf{k}'=\mathbf{k}-\mathbf{q}\mp\frac{1}{2}\mathbf{K}_i$ in Eq. (17) and that six domains for $\mathbf{k}$ and six domains for $\mathbf{k}'$ are the inversion of those depicted by Figs. 3(a) and 3(b), respectively. Then, replacing $\mathbf{r}$ by $-\mathbf{r}$ in Eq. (17) and observing that $u_{\mathbf{k}}(-\mathbf{r})$ and $v_{\mathbf{k}'}{}^*(-\mathbf{r})$ are, respectively, equal to $u_{-\mathbf{k}}(\mathbf{r})$ and $v_{-\mathbf{k}'}{}^*(\mathbf{r})$ [see Eqs. (16)], one finds an expression with $-\mathbf{k}$ and $-\mathbf{k}'$ in place of $\mathbf{k}$ and $\mathbf{k}'$. Now, invert the sign of $\mathbf{k}$ and $\mathbf{k}'$. Then, one finds the original expression, where $\mathbf{k}$ and $\mathbf{k}'$ are related by $\mathbf{k}'=\mathbf{k}+\mathbf{q}\pm\frac{1}{2}\mathbf{K}_i$ and the domains for $\mathbf{k}$ and $\mathbf{k}'$ are the same as Figs. 3(a) and 3(b). Thus, γ^2 is an even function of $\mathbf{q}$, and we neglect its q^2 dependence.

For the self-consistent gap equation we obtain the same equation as (12), where, however, $\mathbf{k}$ and $\mathbf{k}'$ are related by $\mathbf{k}'=\mathbf{k}+\mathbf{q}\pm\frac{1}{2}i\mathbf{K}_i$. For the total energy of the formation of the SDW we obtain the same expression as Eq. (14), neglecting a small change of the distribution of $\mathbf{k}$ and $\mathbf{k}'$ in $\mathbf{k}$ space in the process of the formation of the SDW. Discussion of the solution will be given also in Sec. VIII.

V. SINUSOIDAL SDW

For a sinusoidal SDW we assume the exchange potential in the form

$$2V(\mathbf{r})\sigma_x\cos\mathbf{q}\cdot\mathbf{r}, \quad (25)$$

where $V(\mathbf{r})$ is a real function having an antiferromagnetic pattern and tetragonal symmetry as we assume

q to be parallel to [001] (and small). A factor of 2 is used just for the sake of convenience, but it makes us write the matrix element of (25) as $V_{kk'}$ with the definition of (5). The potential (25) connects $\phi_{ak}\alpha$ to both $\phi_{bk'}\beta$ and $\phi_{bk''}\beta$, where $\mathbf{k'}\equiv\mathbf{k}-\mathbf{q}\pm\frac{1}{2}\mathbf{K}_i$ and $\mathbf{k''}\equiv\mathbf{k}+\mathbf{q}\pm\frac{1}{2}\mathbf{K}_i$. It connects $\phi_{bk'}\beta$ further to $\phi_{ak'''}\alpha$, with $\mathbf{k'''}\equiv\mathbf{k}-2\mathbf{q}$, and $\phi_{bk''}\beta$ to $\phi_{ak''''}\alpha$, with $\mathbf{k''''}\equiv\mathbf{k}+2\mathbf{q}$, and so on. Here α and β may be interchanged. Thus, we have to do with a matrix of infinite dimension. However, even if we had solved the problem of diagonalizing this infinite matrix, we still have a difficulty. The spin density that we would obtain with the use of the exact eigenfunctions would contain harmonics having wave vectors 2**q**, 3**q**, etc., so that the starting potential of the form of (25) would not be valid. In order to obtain a SDW in a self-consistent way, we have to start with an exchange potential containing harmonics of indefinite amplitudes and have to work out self-consistent equations to determine these amplitudes.

We assume that harmonics in the SDW are small and start with (25). We take exactly into account the interaction between two Bloch states, one in band a and the other in band b, when their energies, $\epsilon_a(\mathbf{k})$ and $\epsilon_b(\mathbf{k'})$, are nearly equal to each other, but we take the neighboring two states with $\epsilon_b(\mathbf{k''})$ and $\epsilon_a(\mathbf{k'''})$ as perturbing the former two. Here either

$$\mathbf{k'}\equiv\mathbf{k}-\mathbf{q}+\tfrac{1}{2}\mathbf{K}_z=\mathbf{k}+\mathbf{Q},\ \mathbf{k''}\equiv\mathbf{k}-\mathbf{Q},\ \mathbf{k'''}\equiv\mathbf{k}+2\mathbf{Q} \quad (26)$$

or

$$\mathbf{k'}\equiv\mathbf{k}+\mathbf{q}-\tfrac{1}{2}\mathbf{K}_z=\mathbf{k}-\mathbf{Q},\ \mathbf{k''}\equiv\mathbf{k}+\mathbf{Q},\ \mathbf{k'''}\equiv\mathbf{k}-2\mathbf{Q}. \quad (27)$$

Furthermore, in the spin density function we neglect harmonics. Thus, we set up a self-consistency equation only for $V(\mathbf{r})$ of (25), or for its matrix element $V_{kk'}$ which we put again to be a constant, g. This approximate treatment will not be valid for $\mathbf{q}\rightarrow0$, unless g tends to zero at the same time.

We have then to solve the following secular equation:

$$\begin{vmatrix} \epsilon_b(\mathbf{k''})-E & g & 0 & 0 \\ g & \epsilon_a(\mathbf{k})-E & g & 0 \\ 0 & g & \epsilon_b(\mathbf{k'})-E & g \\ 0 & 0 & g & \epsilon_a(\mathbf{k'''})-E \end{vmatrix}=0. \quad (28)$$

Taking states $\mathbf{k''}$ and $\mathbf{k'''}$ as perturbations, we obtain energy eigenvalues up to order g^2 as follows:

$$E=\tfrac{1}{2}(\epsilon_a+\epsilon_b')\pm(x^2+g^2)^{1/2}-\tfrac{1}{2}g^2(\epsilon_a'''-\epsilon_b')^{-1}$$
$$-\tfrac{1}{2}g^2(\epsilon_b''-\epsilon_a)^{-1}\pm\tfrac{1}{2}g^2x(x^2+g^2)^{-1/2}$$
$$\times[(\epsilon_a'''-\epsilon_b')^{-1}-(\epsilon_b''-\epsilon_a)^{-1}]. \quad (29)$$

Here $\epsilon_a(\mathbf{k})$, $\epsilon_b(\mathbf{k'})$, etc., have been abbreviated as ϵ_a, ϵ_b', etc., and x is defined by Eq. (15). The expression (29) is valid when $\epsilon_a'''-\epsilon_b'$ and $\epsilon_b''-\epsilon_a$ are much greater than g. This condition may not be satisfied for some $\mathbf{k}$ for which $\epsilon_a'''-\epsilon_b$ or $\epsilon_b''-\epsilon_a$ vanishes or becomes small. Still, (29) can be used when we take a sum over such $\mathbf{k}$, by taking the principal value.
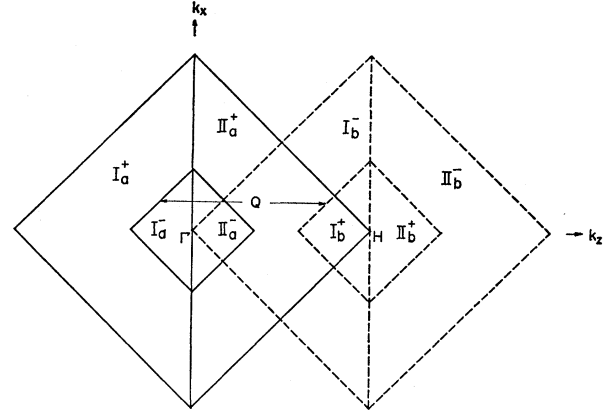

FIG. 4. Partition of the Brillouin zone for band a: $I_a^\pm$ for the left half, $II_a^\pm$ for the right half, $\pm$ representing outside and inside the Fermi surface. Also, partition of the displaced Brillouin zone for band b with similar notation. These partitions are for convenience in the calculation of the sinusoidal SDW.

To decide which of (26) and (27) is to be used, we divide the Brillouin zone into four regions, I_a^-, I_a^+, II_a^-, II_a^+, for band a, as shown in Fig. 4, where I and II refer to the negative and positive sides of the k_z axis, respectively, and $\mp$ indicate the regions of negative and positive energies, i.e., inside and outside the Fermi surface. We also divide the Brillouin zone displaced by $\frac{1}{2}\mathbf{K}_z$ for band b into four regions, I_b^-, I_b^+, II_b^-, II_b^+, with a similar meaning. Q ($=\frac{1}{2}K_z-q$) is the distance between parallel Fermi surfaces as shown in Fig. 4. Then, when **k** is in I_a^-, $\mathbf{k'}=\mathbf{k}+\mathbf{Q}$ is in I_b^+, and when $\mathbf{k'}$ is in I_b^-, $\mathbf{k}=\mathbf{k'}-\mathbf{Q}$ is mostly in I_a^+, some of $\mathbf{k}\equiv\mathbf{k'}-\mathbf{Q}$ being in other regions. In these cases we may assume (26) and take the lower branch of the energy (29). Considering in a similar way in other cases, we assume as follows:

When either **k** is in I_a^- or $\mathbf{k'}$ is in I_b^-, we assume (26) and take the lower energy branch. When **k** is in I_a^+ or $\mathbf{k'}$ is in I_b^+, we also assume (26) but take the upper energy branch. When either **k** is in II_a^- or $\mathbf{k'}$ is in II_b^-, we assume (27) and take the lower energy branch. When **k** is in II_a^+ or $\mathbf{k'}$ is in II_b^+, we also assume (27) but take the upper energy branch.

Corresponding to the secular equation (28), we obtain eigenfunctions in the following forms:

$$\psi_k=A_k\phi_{ak}\alpha+B_{k'}\phi_{bk'}\beta+C_{k''}\phi_{bk''}\beta+D_{k'''}\phi_{ak'''}\alpha,$$
$$\quad (30)$$

$$\psi_{k'}=A_k\phi_{ak}\beta+B_{k'}\phi_{bk'}\alpha+C_{k''}\phi_{bk''}\alpha+D_{k'''}\phi_{ak'''}\beta.$$

Here the coefficients are all real. The spin density is

$$S(\mathbf{r})=\sum_{\text{occ.}}[\psi_k^*\cdot(\tfrac{1}{2}\sigma_x)\psi_k+\psi_{k'}^*\cdot(\tfrac{1}{2}\sigma_x)\psi_{k'}]=\sum_{\text{occ.}}\psi_k^*\cdot\sigma_x\psi_k$$

$$=\sum_{\text{occ.}}\{A_kB_{k'}\exp[i(\mathbf{k}-\mathbf{k'})\cdot\mathbf{r}]u_kv_{k'}^*$$

$$+A_kC_{k''}\exp[i(\mathbf{k''}-\mathbf{k})\cdot\mathbf{r}]u_k^*v_{k''}$$

$$+B_{k'}D_{k'''}\exp[i(\mathbf{k'}-\mathbf{k'''})\cdot\mathbf{r}]u_{k'''}^*v_{k'}$$

$$+\text{c.c.}+\cdots\}. \quad (31)$$

The three terms written explicitly in (31) are proportional to $\exp(i\mathbf{q}\cdot\mathbf{r})$ if Eqs. (26) are used or proportional to $\exp(-i\mathbf{q}\cdot\mathbf{r})$ if Eqs. (27) are used. Terms represented by dots are harmonics which are proportional to $\exp(\pm 2i\mathbf{q}\cdot\mathbf{r})$ or $\exp(\pm 3i\mathbf{q}\cdot\mathbf{r})$; they will be neglected. As before, we multiply $S(\mathbf{r})$ by $-J\phi_{a\kappa}{}^{*}\phi_{b\kappa'}$, integrate, and put the result equal to $V_{\kappa\kappa'}$, or g [the integral of $2V(\mathbf{r})$ $\cos\mathbf{q}\cdot\mathbf{r}$ times $\phi_{a\kappa}{}^{*}\phi_{b\kappa'}$ is $V_{\kappa\kappa'}$ if we define the latter by Eq. (5)]. In the process of this calculation, if we assume Eqs. (26) and put $\mathbf{k}'=\mathbf{k}-\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_i$ and $\mathbf{\kappa}'=\mathbf{\kappa}-\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_j$, we obtain integrals

$$\int \exp[\tfrac{1}{2}i(\mp\mathbf{K}_i\pm\mathbf{K}_j)\cdot\mathbf{r}]u_{\mathbf{k}}v_{\mathbf{k}'}{}^{*}u_{\kappa}{}^{*}v_{\kappa'}d\mathbf{r},$$

$$\int \exp[\tfrac{1}{2}i(\pm\mathbf{K}_i\pm\mathbf{K}_j)\cdot\mathbf{r}]u_{\mathbf{k}}{}^{*}v_{\mathbf{k}''}u_{\kappa}{}^{*}v_{\kappa'}d\mathbf{r},$$

$$\int \exp[\tfrac{1}{2}i(\pm\mathbf{K}_i\pm\mathbf{K}_j)\cdot\mathbf{r}]u_{\mathbf{k}'''}{}^{*}v_{\mathbf{k}'}u_{\kappa}{}^{*}v_{\kappa'}d\mathbf{r}.$$

(Here the $\mathbf{K}_i$'s appearing in the three integrals are not necessarily the same. The relation $\mathbf{k}'=\mathbf{k}-\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_i$ means that $\pm\tfrac{1}{2}\mathbf{K}_i$ is so chosen that both $\mathbf{k}$ and $\mathbf{k}'$ are within the Brillouin zone; this applies for the first integral. In the second integral, $\pm\tfrac{1}{2}\mathbf{K}_i$ corresponds to $\mathbf{k}''-\mathbf{k}=\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_i$, both $\mathbf{k}$ and $\mathbf{k}''$ being in the Brillouin zone. In the third integral, $\pm\tfrac{1}{2}\mathbf{K}_i$ comes from $\mathbf{k}'-\mathbf{k}'''=\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_i$, both $\mathbf{k}'$ and $\mathbf{k}'''$ being in the Brillouin zone.) We replace all these integrals by the constant γ^2 defined by Eq. (17). This replacement is justified in the case of well-localized Wannier functions, as we have shown in Sec. III. In a more general case, we may put $\mathbf{q}=0$ and take an appropriate average over the wave vectors. The errors to be introduced by putting $\mathbf{q}=0$ should be of order q^2, since a sinusoidal SDW does not change by reversing the sign of $\mathbf{q}$ (and the self-consistency equation to be derived below does not depend on the sign of $\mathbf{q}$). One might be worried about whether or not the second and third integrals would yield positive real values, since the asterisk (*) is on both u's. However, on averaging over $\mathbf{k}$ or $\mathbf{k}'$ these vectors pass a point in $\mathbf{k}$ space as well as its inversion point with respect to the origin, so that for instance in the second integral $\mathbf{k}$ and $\mathbf{k}''$ can be replaced by $-\mathbf{k}$ and $-\mathbf{k}''$, respectively, and $u_{-\mathbf{k}}{}^{*}v_{-\mathbf{k}''}$ can be converted to $u_{\mathbf{k}}v_{\mathbf{k}''}{}^{*}$ by Eqs. (16). In the case where we put $\mathbf{\kappa}'=\mathbf{\kappa}+\mathbf{q}\pm\tfrac{1}{2}\mathbf{K}_j$, we obtain integrals of the same forms but of different values if we are to be exact. However, in the present approximation they are the same.

The three integrals are the coefficients of $A_{\mathbf{k}}B_{\mathbf{k}'}$, $A_{\mathbf{k}}C_{\mathbf{k}''}$, and $B_{\mathbf{k}'}D_{\mathbf{k}'''}$, respectively, in the expression for the matrix element of $S(\mathbf{r})$. Thus, we obtain the self-consistency equation as

$$g=-J\gamma^2 \sum_{\text{occ.}} [A_{\mathbf{k}}B_{\mathbf{k}'}+A_{\mathbf{k}}C_{\mathbf{k}''}+B_{\mathbf{k}'}D_{\mathbf{k}'''}]. \quad (32)$$

$A_{\mathbf{k}}B_{\mathbf{k}'}$ is essentially the same as (9), with $V_{\mathbf{k}\mathbf{k}'}$ replaced by g, but it contains an extra term arising from the perturbation calculation. The remaining two terms in Eq. (32) are due to the perturbation. Neglecting second-order quantities of $g/(\epsilon_a{}'''-\epsilon_b{}')$ and $g/(\epsilon_b{}''-\epsilon_a)$ compared with unity, we obtain the final result[18]

$$g=\tfrac{1}{2}J\gamma^2 g \sum_{\text{occ.}} \{\mp(x^2+g^2)^{-1/2}+(\epsilon_a{}'''-\epsilon_b{}')^{-1}+(\epsilon_b{}''-\epsilon_a)^{-1}$$

$$\mp x(x^2+g^2)^{-1/2}[1-\tfrac{1}{2}g^2/(x^2+g^2)]$$

$$\times[(\epsilon_a{}'''-\epsilon_b{}')^{-1}-(\epsilon_b{}''-\epsilon_a)^{-1}]\}. \quad (33)$$

When we compare this equation with Eq. (12), which is applicable to antiferromagnetic and helical SDW's, we find an extra factor of $\tfrac{1}{2}$ in the right side of Eq. (33) besides terms arising from perturbation calculations. However, in the sinusoidal case, half of the Fermi surface of band a, lying on the side of negative k_z, interacts with the same side of the Fermi surface of band b situated at [001], and the remaining half of the Fermi surface of band a interacts with the corresponding side of the Fermi surface of band b situated at [00$\bar{1}$], so that the Fermi surface of band a vanishes completely. A similar situation occurs with the Fermi surface of band b, although this may not vanish completely because this is larger. In the case of a helical SDW such vanishing occurs only on one side of the Fermi surface. Since those values of $\mathbf{k}$ for which x vanishes or x is of order of g make main contribution to the sum in Eq. (33) through the first term, we have about the same equation for the sinusoidal SDW as for the helical SDW, the factor $\tfrac{1}{2}$ being nearly cancelled because of the situation mentioned above. Thus, we obtain about the same value of g in these two cases. However, the energy of formation of the SDW, which is negative, is about twice as large in the sinusoidal case as in the helical case due to the same situation. Hence, the sinusoidal SDW is more stable than the helical SDW. We will show these facts by numerical computations in Sec. VIII.

Neglecting a small change in the distribution of occupied $\mathbf{k}$'s in going from the paramagnetic state to the SDW state, we obtain the energy of the formation of the sinusoidal SDW as

$$E_{\text{SDW}}=\sum_{\text{occ.}} \{2E_{\mathbf{k}}{}^{\pm}-\tfrac{1}{2}[\langle\psi_{\mathbf{k}}{}^{*}|2V(\mathbf{r})\sigma_x \cos\mathbf{q}\cdot\mathbf{r}|\psi_{\mathbf{k}}\rangle$$

$$+\langle\psi_{\mathbf{k}'}{}^{*}|2V(\mathbf{r})\sigma_x \cos\mathbf{q}\cdot\mathbf{r}|\psi_{\mathbf{k}'}\rangle]\}$$

$$-\sum_{\text{occ.}} 2[\epsilon_a(\mathbf{k})+\epsilon_b(\mathbf{k})], \quad (34)$$

where $E_{\mathbf{k}}{}^{\pm}$ represent the upper and lower branches of the energy (29). The potential energy term in Eq.

[18] K. Motizuki, A. Shibatani, and T. Nagamiya, J. Appl. Phys. 39, 1098 (1968). Equation (6) of this reference differs from Eq. (33) of the present paper in that the former lacks the term $-(\tfrac{1}{2})g^2/(x^2+g^2)$ which appears in the latter. We shall discuss this point in Sec. VIII.

(34), i.e., the last two terms in curly brackets, is equal to $2g(A_kB_{k'}+A_kC_{k''}+B_{k'}D_{k'''})$, and the final result is

$$E_{SDW}=2\sum_{occ.}\mp\{|x|-(x^2+g^2)^{1/2}+\tfrac{1}{2}g^2(x^2+g^2)^{-1/2}$$

$$-\tfrac{1}{4}g^4x(x^2+g^2)^{-3/2}[(\epsilon_a'''-\epsilon_b')^{-1}-(\epsilon_b''-\epsilon_a)^{-1}]\}. \quad (35)$$

VI. ROLE OF RESERVOIR

Band calculations[15] show that a high density of states is associated with the third band which we called the reservoir in Sec. II. The density of states of this band at the Fermi surface, which will be denoted by ρ (ρ/N per atom), seems to be 2.4 times the total density of states of bands a and b at their Fermi surfaces. In the process of the formation of a SDW, a certain number n of electrons will flow from the reservoir to the bands a and b. The Fermi level of the reservoir will be depressed by $n/2\rho$, since there are both spins, and the work needed to remove n electrons from the reservoir will be $\tfrac{1}{2}n(n/2\rho)$ $=n^2/4\rho$. If no SDW is yet formed, the Fermi level of the bands a and b will be elevated from $\epsilon_F(=0)$ to a certain value ϵ_F'. Using the energy spectra given by Eqs. (1) and (2) and assuming that k_e and k_h have changed to k_e' and k_h', we have

$$\epsilon_F'=\alpha(k_e'-k_e)=\beta(k_h-k_h'). \quad (36)$$

We shall denote $k_h-k_e=\delta_0$ and $k_h'-k_e'=\delta$. The density of states of band a and that of band b are, respectively, $(V/8\pi^3)4k^2/\alpha$ and $(V/8\pi^3)4k^2/\beta$, where $V=\tfrac{1}{2}Na^3$ is the total volume and k, as before, the distance from the center of the respective octahedron to the corners of it. Hence,

$$n=2\frac{V}{8\pi^3}\left[\int_0^{\epsilon_f'}4k^2\frac{d\epsilon_a}{\alpha}+\int_0^{\epsilon_f'}4k^2\frac{d\epsilon_b}{\beta}\right]$$

$$=\frac{V}{\pi^3}\left[\int_{k_e}^{k_e'}k^2dk+\int_{k_h'}^{k_h}k^2dk\right]$$

$$=\frac{V}{3\pi^3}[(k_e'^3-k_e^3)+(k_h^3-k_h'^3)]. \quad (37)$$

k_e' and k_h' are determined from Eqs. (36) and (37) for a given value of n.

The energy required to fill the bands a and b by n electrons and to evaluate the Fermi level from zero to ϵ_F' is

$$\frac{V}{4\pi^3}\left[\int_{k_e}^{k_e'}4k^2\alpha(k-k_e)dk+\int_{k_h'}^{k_h}-4k^2\beta(k-k_h)dk\right]$$

$$=\frac{V}{4\pi^3}\{\alpha[(k_e'^4-k_e^4)-\tfrac{4}{3}k_e(k_e'^3-k_e^3)]$$

$$+\beta[(k_h'^4-k_h^4)-\tfrac{4}{3}k_h(k_h'^3-k_h^3)]\}. \quad (38)$$

The sum of this energy and $n^2/4\rho$ is the energy required to transfer n electrons from the reservoir to the bands

a and b. We will denote it by $E_{transfer}$. We now construct a SDW, antiferromagnetic, helical, or sinusoidal, using k_e' and k_h' in place of k_e and k_h and in the way described in previous sections. The formation energy will be denoted by E_{SDW} as before. Then $E_{SDW}+E_{transfer}$ is the change of the energy of the whole system, which we will denote by ΔE. This ΔE is plotted as a function of $k_h'-k_e'=\delta$, with $k_h-k_e=\delta_0$ as a parameter, and the lowest minimum is looked for. By this minimizing process we can determine the value of δ, and hence of n, and we are assured of the equalness of the Fermi level of the reservoir and that of the bands a and b. The value of δ is the value of the wave number q ($=2\pi/a$ $-Q$) of the SDW in the helical and sinusoidal cases. In the antiferromagnetic case, the wave number is always $2\pi/a$.

VII. NÉEL TEMPERATURE

For finite temperatures we have the Fermi distribution factor in the self-consistency gap equation. In this paper we discuss only the Néel temperature where the gap g tends to zero. We assume the transition of the second order.

The wave number of the infinitesimal SDW that sets in at T_N is not necessarily the same as that for $T=0$. It is determined by minimizing the free energy. But instead of minimizing the free energy, we may find the wave number by maximizing T_N. Another problem we should be concerned with is whether there is a flow of electrons from the reservoir to the bands a and b at T_N. In the process of the formation of an infinitesimal SDW, the flow also should be infinitesimal, and we may neglect it. However, if we consider separately the reservoir and the system of band a and band b, then we would find that the Fermi level of the reservoir varies with temperature in a different way from the Fermi level of the system of band a and band b, in the paramagnetic state. The temperature dependence of the Fermi level is known to be given by the equation

$$\epsilon_F(T)=\epsilon_F(0)-\tfrac{1}{6}\pi^2\frac{d\rho(\epsilon)}{\rho(\epsilon)d\epsilon}\bigg|_{\epsilon=\epsilon_f(0)}\cdot(kT)^2, \quad (39)$$

and although we do not know the value of the coefficient of the second term for the reservoir, the Fermi level of the reservoir must decrease with rising temperature, since the reservoir has electron-type Fermi surfaces so that its density of states, $\rho(\epsilon)$, is an increasing function of ϵ. On the other hand, for the system of band a and band b we have

$$d\rho(\epsilon)/\rho(\epsilon)d\epsilon=2(k_e/\alpha^2-k_h/\beta^2)/(k_e^2/\alpha+k_h^2/\beta), \quad (40)$$

according to our assumption, and although this seems to be positive also, since k_e and k_h are not much different from each other but a larger value of β than α appears to be appropriate for pure Cr, its value can be different from the value for the reservoir. Thus, to equalize

the Fermi levels, a flow of electrons may occur between the two systems when they are in the paramagnetic state and there is a variation in temperature. Since we do not know exactly what the real situation is, we shall simply neglect the possible flow. A discussion on this point will be given in Sec. IX.

In the limit of vanishing g, the energy eigenvalues reduce to the unperturbed values $\epsilon_a(\mathbf{k})$ and $\epsilon_b(\mathbf{k}')$. The Fermi distribution function is the function of these energies. The self-consistency equations (12) and (33), with the Fermi distribution factor added, reduce to the following one in the limit of $g \to 0$:

$$1 = J\gamma^2 \left[\sum_{\mathbf{k}} \frac{2f[\epsilon_a(\mathbf{k})]}{\epsilon_b(\mathbf{k}') - \epsilon_a(\mathbf{k})} + \sum_{\mathbf{k}'} \frac{2f[\epsilon_b(\mathbf{k}')]}{\epsilon_a(\mathbf{k}) - \epsilon_b(\mathbf{k}')} \right], \quad (41)$$

where $\mathbf{k}' \equiv \mathbf{k} + \mathbf{Q}$ (or $\mathbf{k}' \equiv \mathbf{k} - \mathbf{Q}$) and the summations over $\mathbf{k}$ and $\mathbf{k}'$ extend over band a and band b, respectively. Numerical computations of T_N and discussions will be given in Sec. VIII.

VIII. NUMERICAL RESULTS

In presenting our numerical results, we choose the unit of wave vectors as $2\pi/a$ and the unit of energy as $2\pi\alpha/a$, where α is the coefficient in Eq. (1). Thus, for exact antiferromagnetism we have $Q=1$, instead of $Q=2\pi/a$, and for q which appeared in the discussion of helical and sinusoidal SDW's we have $q=1-Q$. For pure chromium we assume $k_e=0.35$, $k_h=0.40$, $k_h-k_e = 0.05$. These values were adopted by referring to band calculations made by Loucks.[13] From band calculations made by Asano and Yamashita[15] we find k_e somewhere around 0.40 and k_h around 0.44, so that our assumed numerical values might be too small. With our choice of units, Eqs. (1) and (2) become $\epsilon_a(\mathbf{k}) = k - k_e$ and $\epsilon_b(\mathbf{k}) = -\beta(k - k_h)$, respectively, and we choose $\beta = 2$ for most of our calculations, although we made calculations also for $\beta = 1$. The value of β (with $\alpha = 1$) estimated from the slopes of the energy curves given by Asano and Yamashita is approximately 1.5, and the value of β estimated from the ratio of the density of states of band a and that of band b at the paramagnetic Fermi level is 2.4 [the densities of states were derived with the use of their equations in Sec. 4.2 for $\epsilon_1(\mathbf{k})$ and $\epsilon_2(\mathbf{k})$, our $\epsilon_b(\mathbf{k})$ and $\epsilon_a(\mathbf{k})$, respectively, which give spherical Fermi surfaces but are good to give densities of states at the Fermi level, the Fermi level being at -0.007 Ry]. Thus, $\beta = 2$ may not be unreasonable. For $\beta = 1$ we found qualitatively the same results.

For our linear energy spectra of bands a and b, the density of states per atom of both bands for both spins is $2\rho_{a+b}/N = 4(k_e^2 + k_h^2/\beta) = 0.81$ for $k_e = 0.35$, $k_h = 0.40$, and $\beta = 2$. The energy unit here is $2\pi\alpha/a$, whose value is 0.35 Ry as estimated from the slopes of the energy curves given by Asano and Yamashita. Thus, our $2\rho_{a+b}/N$ is 2.3 Ry^{-1}, whereas they give a value of 3.5 Ry^{-1}. The discrepancy is partly due to our smaller values of k_e and k_h. They also give $2\rho/N = 8.5$ Ry^{-1} for

the reservoir, so that $\rho/\rho_{a+b} = 2.4$. This ratio is important in discussing electron flows from the reservoir to bands a and b and in discussing alloys. We will take several values for ρ, including $2\rho/N = 2$, i.e., $\rho/\rho_{a+b} = 2/0.81 = 2.47$.

The value of g, half the energy gap in the SDW band, that we obtain for the sinusoidal SDW in pure chromium will be 0.048 eV (0.010 in our energy unit). We will, therefore, pay attention to values of g in the neighborhood of 0.01. Our perturbational calculation for the sinusoidal case should not be good for large values of g, particularly when $k_h - k_e = \delta_0$ or $k_h' - k_e' = \delta$ is small; the smaller the value of δ_0 or δ, the smaller is the value of g that we have to consider in order to make our perturbational calculation valid. In the limit of vanishing δ_0 or δ no values of g, except zero, should be acceptable. In this connection, we should like to refer to erroneous equations that we have reported in our preliminary publication[18] in place of Eqs. (33) and (35) of the present paper. The term $-\frac{1}{2}g^2/(x^2 + g^2)$ in the middle of the right side of Eq. (33) and the last term in Eq. (35) have been lacking. These terms arise from an extra term in $A_{\mathbf{k}}B_{\mathbf{k}'}$ due to the perturbation. However, if we neglect these terms, the gap equation and E_{SDW} for the sinusoidal reduce to those for the antiferromagnetic SDW in the limit of vanishing δ_0 or δ. (The helical SDW reduces obviously to the antiferromagnetic SDW in this limit.) This reduction is a desirable property of the equations and suggests the usefulness of the erroneous equations for their being semitheoretically correct. Furthermore, the numerical results that we reported, which were based on such equations, are only slightly different from those obtained with correct equations in the most important range of parameter values, there being no qualitative difference. For this reason we shall also show here [in Fig. 5(a)] a result obtained with the semitheoretical equations.

Our results are summarized as follows:

(a) *The gap g.* Solving Eqs. (12) and (33), we obtain curves shown in Figs. 5(a) and 5(b). Here $1/u = 2/J\gamma^2 N$ is plotted as a function of g for several values of δ_0. In Fig. 5(a) the curves for the sinusoidal SDW are based on the semitheoretical equations mentioned above, whereas the curves in Fig. 5(b) are based on Eq. (33). In the neighborhood of $g = 0.01$ and for large values of δ_0, these two sets of curves agree well with each other, and they are consistently higher than the curves for the helical and antiferromagnetic SDW's. This would suggest that the sinusoidal SDW is the most stable. In fact, we find that the formation energy E_{SDW}, which is negative, is nearly twice as large for the sinusoidal SDW as for the helical SDW, as was mentioned in Sec. V. The antiferromagnetic SDW is the least stable. For this SDW the curves tend to finite values for $g \to 0$, which means that no antiferromagnetic SDW exists unless $1/u$ has smaller values than these limiting values.

(b) *The total energy and the wave number* q. Corresponding to the relation between $1/u$ and g as shown in Figs. 5(a) and 5(b), we have calculated E_{SDW} by Eq. (14) and Eq. (35) as a function of δ_0 for several $1/u$ values in the vicinity of $1/u=4$. This will not be shown here. The wave number of the helical or sinusoidal SDW q is equal to δ_0 in this case. As mentioned already, the sinusoidal SDW has the lowest value of E_{SDW} for given values of $1/u$ and δ_0, so that we shall be concerned only with the sinusoidal SDW. Even when we consider a flow of electrons from the reservoir, we find that the sinusoidal SDW has the lowest energy.

We have calculated $E_{transfer}$, discussed in Sec. VI. This is the increase in energy associated with a transfer of electrons from the reservoir to the bands a and b, and thus with a change of k_h-k_e from its initial value δ_0 to another value δ. The sum of the value of E_{SDW} for δ and the value of $E_{transfer}$, i.e., $\Delta E = E_{SDW}+E_{transfer}$, is plotted as a function of δ, with δ_0 as a parameter. The results are shown in Figs. 6(a), 6(b), and 6(c), for $\beta=2$, $1/u=4$, and $2\rho/N=1$, 2, and 5. $2\rho/N$ is the density of states of the reservoir including both spins, and its value of 2 seems to be appropriate for chromium. (In our previous paper,[18] we wrote ρ/N for $2\rho/N$ and k_d for δ_0, and a figure that corresponds to Fig. 6(c) was shown. The calculations were based on what we called in this section the "semitheoretical" equations. There was also a slight error in the calculation of $E_{transfer}$, which is not serious. We see that no qualitative change is found in the present new calculations.)

In Fig. 6(a) we find a minimum in each energy curve. The value of δ for this minimum should be the value of q of the stable SDW. In Figs. 6(b) and 6(c), we find two minima for larger values of δ_0. Hence, plotting the lowest minimum, we find a jump in q at a certain value of δ_0. A simple physical meaning of this jump is not seen at this moment. In Figs. 7 and 8 are shown the values of q and g as functions of δ_0.

(c) *Alloys of Cr with Mn and V.* We assume the rigid-band model. When the number of $3d$ electrons increases by an addition of Mn or decreases by an addition of V, the increase or decrease will be distributed among the band a, the band b, and the reservoir in the ratio of their densities of states. Assuming $2\rho_{a+b}/N$ $=0.81$ and some values for $2\rho/N$, we can calculate the change of the Fermi level in the paramagnetic state and hence the changes of k_e and k_h. Thus we can plot q and g as functions of atomic percentage of Mn. Figure 9 shows the plot of $Q=1-q$ calculated in this way. Negative concentrations correspond to V. A jump in q appears at 1.5 at.% of Mn. Experimental observations by Koehler *et al.*[3] show a jump or a steep increase at 0.4~0.5 at.% of Mn.

(d) *The Néel temperature* T_N. The Néel temperature is obtained by solving Eq. (41) for T, contained in the Fermi distribution function. It is still a function of q. We maximize it by varying q. The results are shown in Fig. 10, together with the temperature obtained by
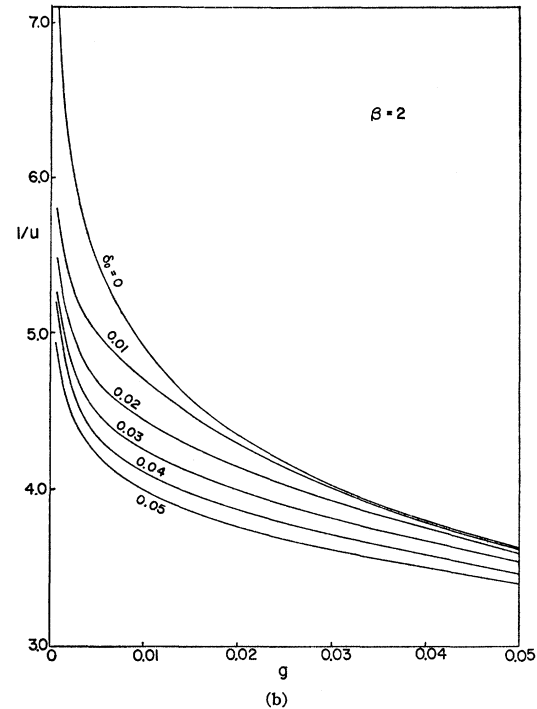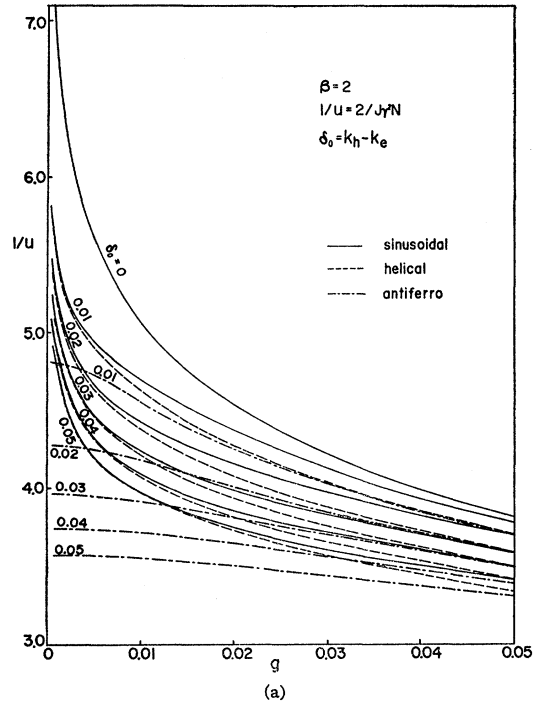

(a)

(b)

FIG. 5. (a) Relation between the gap g and the exchange parameter $1/u$ for three types of SDW, calculated with the use of Eq. (12) for antiferromagnetic and helical SDW's and with the use of an equation similar to Eq. (33), but without a term $-(\frac{1}{2})g^2/(x^2+g^2)$, for sinusoidal SDW. For antiferromagnetic SDW a critical value of $1/u$ is found for $g\to 0$. The value of g for a given $1/u$ is consistently the highest for sinusoidal SDW. The units used are described at the top of Sec. VIII. (b) The g-$(1/u)$ relation for sinusoidal SDW based on Eq. (33). The value of g for a given $1/u$ is higher than those for antiferromagnetic and helical SDW's when g does not exceed about 0.02 in units of $2\pi a/a$, as can be seen by comparison with (a).
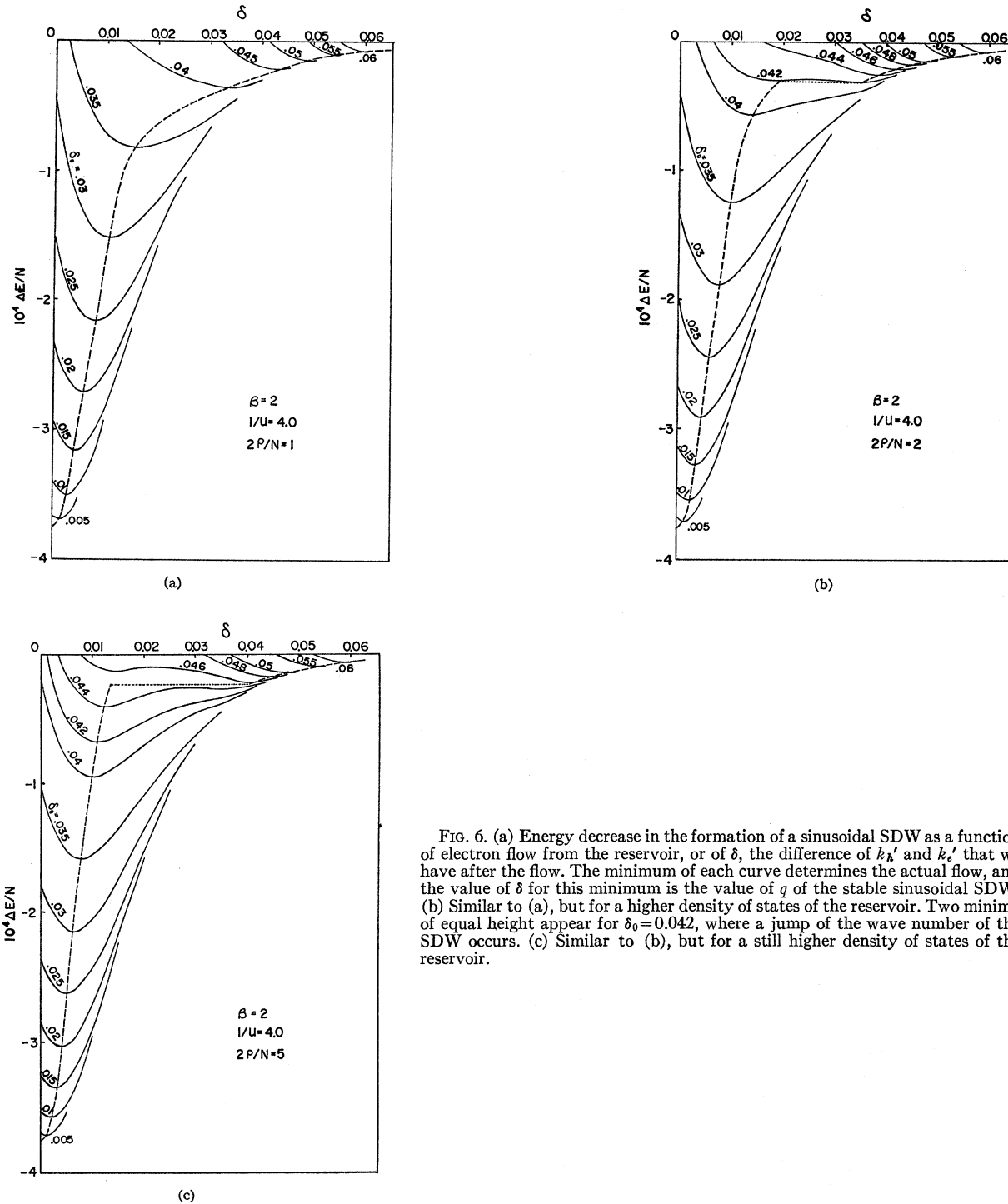
(a)

(b)

(c)

FIG. 6. (a) Energy decrease in the formation of a sinusoidal SDW as a function of electron flow from the reservoir, or of δ, the difference of k_h' and k_e' that we have after the flow. The minimum of each curve determines the actual flow, and the value of δ for this minimum is the value of q of the stable sinusoidal SDW. (b) Similar to (a), but for a higher density of states of the reservoir. Two minima of equal height appear for $\delta_0 = 0.042$, where a jump of the wave number of the SDW occurs. (c) Similar to (b), but for a still higher density of states of the reservoir.

fixing q at δ_0. For $1/u = 3.6$ we see that the antiferromagnetic order, with $q=0$, gives the highest Néel temperature for the range of δ_0 computed, as shown by the uppermost curve; this curve bends down and continues to another branch of negative slope, so that T_N is two-valued in the range of $\delta_0 = 0.06$ to 0.05. For higher values of $1/u$ the Néel temperature of the sinusoidal order (which is the same as that of the helical order) with $q \neq 0$ branches off from the curve of the antiferromagnetic T_N, and this is shown by chain curves; the branching point is situated near (but not exactly at) the point of infinite slope on the curve of the anti-
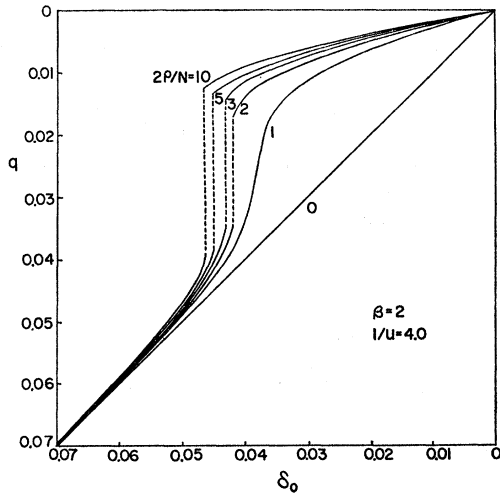
FIG. 7. Wave number q ($=1-Q$) of the sinusoidal SDW as a function of δ_0, the size difference of the electron and hole octahedra in paramagnetic state. The density of states of the reservoir is the parameter.

ferromagnetic T_N. Assuming $\delta_0=0.05$ for pure chromium, we obtain $T_N=600°$K and $q=0.038$ for $1/u=3.8$, and $T_N=278°$K and $q=0.047$ for $1/u=4.0$, the observed T_N and q being $310°$K and 0.037, respectively. Since an appropriate value of $1/u$ for understanding experimental data for $T=0$ is in the neighborhood of 4.0, our calculations concerning T_N give results consistent with those for $T=0$ in explaining experimental data.

In all curves of T_N for the antiferromagnetic order it is seen that T_N is a two-valued function of δ_0 in a certain range of the latter. The mathematical reason for this is as follows: When we calculate $1/u\equiv 2/J\gamma^2 N$ from Eq. (41) as a function of T, instead of calculating T as
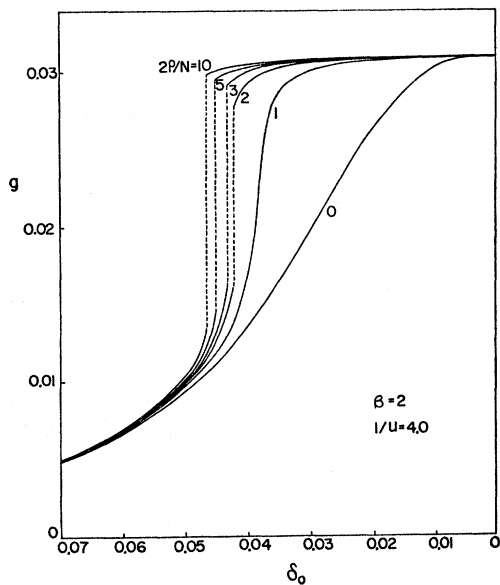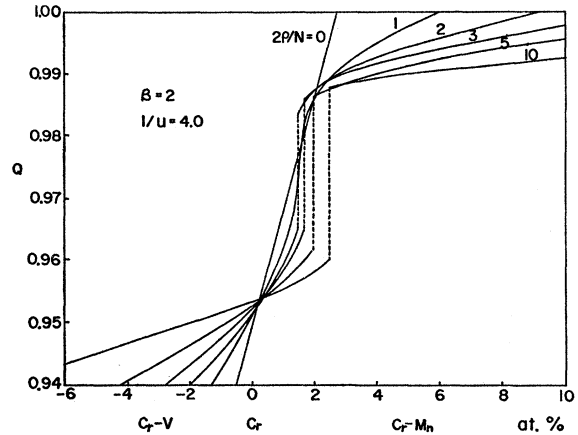

FIG. 8. Energy gap g corresponding to Fig. 7.

FIG. 9. Wave number Q of the sinusoidal SDW, plotted as a function of alloy concentration. The rigid-band model is assumed. The density of states of the reservoir is taken as a parameter.

a function of $1/u$, terms with $\epsilon_b(\mathbf{k}')>\epsilon_a(\mathbf{k})$ give positive contributions to the first sum and terms with $\epsilon_b(\mathbf{k}')<\epsilon_a(\mathbf{k})$ give negative contributions; the situation is opposite in regard to the second sum. If we use ϵ_c to denote the energy where the two band energies cross, i.e., $\epsilon_c=\epsilon_a(\mathbf{k})=\epsilon_b(\mathbf{k}')$, where $\mathbf{k}'\equiv\mathbf{k}+(2\pi/a,0,0)$ in the antiferromagnetic order, we see that ϵ_c is a positive
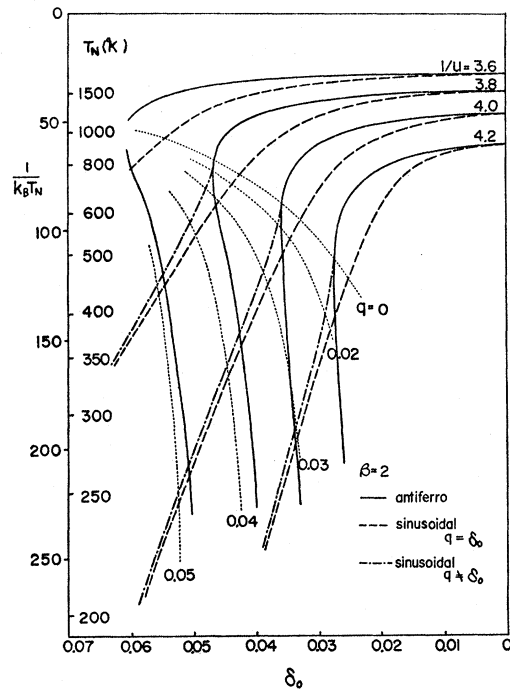

FIG. 10. Reciprocal Néel temperature versus δ_0, the size difference of the electron and hole octahedra in paramagnetic state. In the upper right portion, the Néel temperature of the antiferromagnetic SDW, represented by full curves, is seen to be the highest. In the lower left portion, the Néel temperature of the sinusoidal SDW, represented by chain curves, becomes higher; the corresponding q values are shown. Broken curves are for the sinusoidal SDW with $q=\delta_0$.

TABLE I. Theoretical results in comparison with experimental data. Assumed values of parameters: $\beta=2\alpha$, $2\pi\alpha/a=0.35$ Ry, $2\rho_{a+b}/N=0.81$, $2\rho/N=2$ (the unit of energy for these density of states being 0.35 Ry), $1/u=2/J\gamma^2N=4.0, 3.9, 3.8$.

| | Theoretical | | | Experimental[a,b] |
	$1/u=4.0$	3.9	3.8	
$T=0$:				
Q for Cr	0.952	0.956		0.950
Energy gap for Cr	0.095 eV	0.149 eV		0.136 eV
Mn at.% at jump of Q	1.5%	0.4%		0.4~0.5%
Q before jump	0.965	0.961		0.955
Q after jump	0.983	0.982		0.965
$T=T_N$:				
T_N for Cr	278°K	398°K	600°K	310°K
Q for Cr	0.953	0.955	0.962	0.963
Mn at.% for $Q\rightarrow1$	2.6%	1.8%	0.6%	0.4%
Q before jump to $Q=1$	~0.98	~0.975	~0.97	0.972
T_N for 2 at.% of Mn	455°K	887°K	1190°K	540°K
T_N for 2 at.% of V	193°K	267°K	372°K	150°K

[a] Reference 3 (Koehler et al.), data except for energy gap.
[b] Reference 23, only for energy gap.

quantity. When k_BT is smaller than ϵ_c, we have terms $2f[\epsilon_a(\mathbf{k})]/[\epsilon_b(\mathbf{k}')-\epsilon_a(\mathbf{k})]$, with positive denominator, from excitations of electrons from band a and also negative terms $2\{f[\epsilon_a(\mathbf{k})]-1\}/[\epsilon_b(\mathbf{k}')-\epsilon_a(\mathbf{k})]$, with positive but larger denominator, from holes left in band a, so that the net result is a positive contribution. Thus, with increasing temperature the value of $1/u$ will increase at first. The same is true with band b. When k_BT exceeds ϵ_c, we have terms with negative denominator from excitations of electrons, and since the density of states is higher for higher energies, we can expect a decrease in the value of $1/u$ at sufficiently high temperatures, provided ϵ_c is not too close to the Fermi level, or the difference in size of the electron and hole octahedra is not too small. We then have a maximum in the $1/u$ versus T curve; in other words, T_N as a function of $1/u$ becomes two-valued. Such does not occur in the case of a sinusoidal SDW, since ϵ_c is zero or very small.

We summarize our numerical results in Table I in comparison with the corresponding experimental data. Concerning some disagreement found in this table, we will give discussion in Sec. IX.

IX. COMPARISON WITH EXPERIMENT AND DISCUSSION

Several points of our calculations will be discussed in comparison with experimental observations and considered with the approximations that we have made.

(a) *Critical value of the exchange parameter* $1/u$. We have shown that for absolute zero the sinusoidal SDW has the lowest energy. The energy gap g ($2g$ is the energy gap), obtained by solving the self-consistency equations, was shown in Figs. 5(a) and 5(b) as a func-

tion of $1/u=2/J\gamma^2N$ with δ_0 as a parameter, and we saw that there is a critical value of $1/u$, i.e., the upper limit of $1/u$ for nonvanishing SDW amplitude, only for the antiferromagnetic SDW. In helical and sinusoidal cases, $1/u$ tends to infinity in a logarithmic way as g tends to zero. This divergence comes from our assumption of exact octahedra for the Fermi surfaces of the band a and band b. When one of these Fermi surfaces is displaced by $\mathbf{Q}$ or $-\mathbf{Q}$, they contact each other exactly at least on one side. The real Fermi surfaces are only approximately octahedral so that they cannot be brought into exact contact. In such a case we do not expect the divergence, i.e., we expect the existence of a critical value of $1/u$ even in helical and sinusoidal cases.

(b) *Concentration dependence of Q at $T=0$*. Considering a flow from the reservoir to bands a and b in the process of the formation of a sinusoidal SDW, we found that the value of q or $Q=1-q$ (in units of $2\pi/a$) changes as a function of δ_0 and shows a jump at a certain value of δ_0 that corresponds to the addition of a small amount of Mn to Cr in the rigid-band model, provided the density of states of the reservoir is sufficiently high. However, no jump of Q to 1 is predicted. Neutron diffraction experiment by Koehler et al.[3] at 4.2°K on Cr-Mn, Cr-Re, and Cr-V (and other alloys) shows that the value of Q increases with increasing number of $3d$ (in Re $4d$) electrons; the value is 0.95 at pure Cr, increases to about 0.955 at a concentration of Mn (or Re) of somewhere around 0.35 at.%, and shows a jump or a steep rise by 0.01 to a value of 0.965 at 0.5 at.%. Q increases further slowly with increasing concentration, but above 1.5 at.% all alloys show commensurable antiferromagnetism with $Q=1$, Q changing around this concentration by about 0.03, perhaps in a discontinuous way, although this change has not been measured by changing the concentration continuously. Our theoretical results given in Fig. 9 show for $2\rho/N=2$ a jump of 0.018 from $Q=0.965$ to $Q=0.983$ at 1.5 at. % of Mn, both this jump and the at. % being somewhat too high, but no discontinuous change to $Q=1$. (See also Table I.) $Q=1$ is attained at a much higher concentration that corresponds to $\delta_0=0$, i.e., for the same size of the electron and hole octahedra in the paramagnetic state. This is due to the situation that we found the sinusoidal SDW to be always more stable than the commensurable antiferromagnetic SDW at a given value of the size difference of the two octahedra, provided the hole octahedron is larger. We have not carried out calculations for the opposite case; in the opposite case, i.e., in the case of negative δ_0, an electron flow from the bands a and b to the reservoir may take place, since the higher band is populated after the SDW formation if no flow is allowed. It is possible, therefore, that the state of $Q=1$ persists over a certain range of negative δ_0 from $\delta_0=0$. Furthermore, our perturbational calculation for the sinusoidal

SDW should fail when Q is close to 1, so that the deep minima of the curves of Fig. 6 at small values of δ are not necessarily reliable; they might occur at $\delta=0$, giving $Q=1$, for small values of positive δ_0 if exact calculations were made.

Falicov and Penn,[19] in discussing a problem at absolute zero similar to ours, find a jump of Q to 1. However, their treatment is not based on self-consistent calculations nor on rigorous mathematical formulations. Moreover, they interpolate between the sinusoidal SDW and the commensurable antiferromagnetic SDW without introducing harmonics into the former. To bridge between the two SDW's in a continuous way, we must introduce harmonics; the harmonics grow as Q tends to 1, giving rise to squaring of the sinusoidal curve, and the SDW pattern becomes similar to an antiphase domain pattern of antiferromagnetic domains; the period of such an antiphase pattern grows large, and finally we get a single-domain antiferromagnetic pattern.

Herring[20] in his suggestive article discusses the locking of SDW's to commensurate wave vectors. He mentions that a linearly polarized sinusoidal SDW (by contrast with the helical wave) can feel a preference for rational values of Q by virtue of exchange energy alone. In a simple sinusoidal SDW there are unit cells where no spin density exists and also unit cells where the spin density has its full value, whereas in the commensurate antiferromagnetic SDW every unit cell has the full spin density. For this reason Herring suggests that the latter would have a lower energy, if the Q value of the sinusoidal wave is sufficiently close to one. Intuitively, this suggestion is acceptable. On the other hand, when we consider the situation in wave-vector space, there is a complete fitting together of two Fermi surfaces and the vanishing of the Fermi surfaces in the case of the sinusoidal SDW, whereas for the commensurate antiferromagnetism there is only an over-all incomplete fitting of the two Fermi surfaces. Thus, also intuitively, one may suspect a higher stability of the sinusoidal SDW. It is, therefore, not easy to justify the stability of the commensurate antiferromagnetism on the basis of exchange energy alone. Locking of Q to 1 by anisotropy energy is improbable in the case of a linearly polarized SDW, although this would be possible in the case of a helical wave; this type of locking was discussed earlier by Yoshimori[21] for the case of a helical spin arrangement in the rutile-type lattice (by a suggestion of one of the present authors, T. N.). External parameters, such as pressure, may also lock Q to a commensurate value, as Herring also mentions. Spontaneous locking of this type, by magnetoelastic effect, would be a possibility for chromium; such a locking was
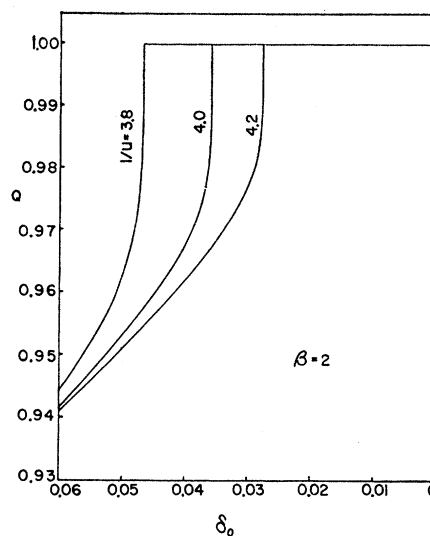

FIG. 11. Q values at the Néel temperature, corresponding to Fig. 10.

discussed in the case of thulium (where the atoms have their intrinsic moments) by Nishikubo and Nagamiya.[22]

An observation[4] at 90°K on Cr-V-Mn also shows a jump of Q at 0.6 at. % of Mn equivalent from 0.96 to 1, the value of Q for the pure Cr being a little higher than 0.95.

(c) *Value of Q at T_N.* Just below T_N, an observation by Koehler et al.[3] shows that the value of Q for the pure Cr is 0.963 and it increases with Mn concentration to 0.972 at 0.35 at.%, where it shows a jump to one. Assuming $\delta_0=0.05$ for the pure Cr, we have results shown in Table I. The dependence of Q on δ_0 is shown in Fig. 11. We see that our results agree with those observed in a reasonable way. However, it must be mentioned that we assumed the same temperature dependence of the Fermi level of the system of bands a and b and that of the reservoir, i.e., we did not consider electron transfer between the two systems. In actuality, some transfer must take place, as was discussed in Sec. VII, from the bands a and b to the reservoir during the heating from 0°K to T_N, so that we have to take a larger value of δ_0 (i.e., on the vanadium side) for T_N than for 0°K, although this cannot be specified quantitatively at the present moment.

(d) *Value of the gap at 0°K.* Calculated values of the gap, $2g$, at 0°K are listed in Table I (0.095 eV for $1/u = 4.0$, 0.149 eV for $1/u = 3.9$, both for the pure Cr). An observation of this gap was made recently by Barker, Halperin, and Rice[23] by measuring the infrared reflectivity of chromium. At 80°K, the absorption maximum occurred at photon energy $5.1kT_N$ ($=0.136$ eV). If this energy is identified with $2g$, then it comes into the

[19] L. M. Falicov and D. R. Penn, Phys. Rev. 158, 476 (1967); J. Appl. Phys. 39, 1103 (1968).
[20] C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV.
[21] A. Yoshimori, J. Phys. Soc. Japan 14, 807 (1959).

[22] T. Nishikubo and T. Nagamiya, J. Phys. Soc. Japan 20, 808 (1965).
[23] A. S. Barker, Jr., B. I. Halperin, and T. M. Rice, Phys. Rev. Letters 20, 384 (1968).

range of our calculated values. Barker *et al.* discussed the effect of electron-phonon scattering on the broadening of the absorption curve and also on the relation between the gap and T_N. As the "unrenormalized" Néel temperature for a model without phonon scattering, they calculated $T_N{}^0 = 750°K$ corresponding to the observed T_N. Our results for T_N, which are based on the complete neglect of the electron-phonon scattering, are closer to the observed value of T_N. However, this fact should not be taken too seriously, since we have made a number of simplifying assumptions.

(e) *Magnetic moment amplitude of the SDW.* We discuss the moment amplitude in the rest of this section. In order to discuss its order of magnitude, we look at Eq. (10b) for the antiferromagnetic case. This equation contains a factor $\exp(\mp\frac{1}{2}i\mathbf{K}_i\cdot\mathbf{r})u_k v_{k'}{}^*$ in the right side, which has come from $\phi_{ak}\phi_{bk'}{}^*$. If the tight-binding approximation is good, then this factor would be $N^{-1}w_a(\mathbf{r})w_b{}^*(\mathbf{r})$ for $\mathbf{R}_n = 0$. The integral of this function within the atomic cell vanishes, since the two Wannier functions are orthogonal. Hence the atomic moment is zero. Even if the tight-binding approximation is not good, the net spin on each atom would be extremely small, as long as we take interband interactions only, as we did.

Our interpretation of the magnetic moment amplitude is as follows: The self-consistent creation of the SDW in chromium is due to the interaction between the electron band and hole band (a and b), and the structure of the present theory need not be altered. However, the main part of the moment arises as the result of intraband interactions and is thus associated with $\phi_{ak}\phi_{ak'}{}^*$, $\phi_{bk}\phi_{bk'}{}^*$, etc. We consider the spin density due to intraband interactions as being induced by the spin density arising from interband interactions and hence proportional to g. Then, what we need is just to reinterpret the meaning of J. This J was a constant which connected the interband spin density to the exchange potential, but now the latter is not only due to the interband spin density but also includes the effect of the intraband spin density whose amplitude is proportional to the amplitude of the interband spin density. Thus, our J should be a very large constant compared with the true J which connects the true spin density to the exchange potential, their ratio being the ratio of the true spin density and the interband spin density.

Although we cannot at present verify this idea by calculations, its correctness is partly supported by the calculation made by Asano and Yamashita[15] for the commensurate antiferromagnetic SDW; namely, they found that the main contribution to atomic moments arises from those states k and k′ which have energy difference much greater than g, i.e., from electrons lying far below the Fermi level.

In this connection, we would like to mention that Asano and Yamashita have overestimated the energy gap and the moment amplitude. They assumed a value of $0.6\mu_B$ for the atomic moment in the antiferromagnetic SDW, which is close to the observed value $0.58\mu_B$ of the maximum moment in the sinusoidal SDW in chromium. However, according to our theory the maximum moment of the sinusoidal SDW is proportional to $2g$, while the moment in the helical and antiferromagnetic SDW's is proportional to g, so that if $0.58\mu_B$ is associated with the sinusoidal SDW, then $0.29\mu_B$ should be the moment in the antiferromagnetic SDW, provided g is the same. Furthermore, since the antiferromagnetic SDW is less stable for chromium, the value of g to be associated with the hypothetical antiferromagnetic SDW should be smaller. In fact, Asano and Yamashita obtained a value of the energy gap of about 0.4 eV, three to four times our values. Conversely, from values 0.1–0.14 eV of the energy gap we would obtain, using the calculation of Asano and Yamashita, moment values of at most $0.15–0.2\mu_B$ for the antiferromagnetic SDW, and $0.3–0.4\mu_B$ (as compared with $0.58\mu_B$) for the sinusoidal SDW.