

## Stability and symmetry of the spin-density-wave state in chromium

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The group-theoretical nonadiabatic Heisenberg model proposed recently by the author for better understanding of the material properties of superconductors is applied to the band structure of chromium. Starting from the symmetry of the Bloch functions of a distinct narrow, roughly half-filled energy band of Cr, it is shown that, within this new model, the electrons may lower their Coulomb correlation energy by forming a state that possesses a spin structure with the space group  $D_{4h}^2$  of perfect antiferromagnetic Cr. We give a general condition for the stability of itinerant antiferromagnetism. The commensurate-incommensurate transition is ascribed, as usual, to the peculiar geometric features of the Fermi surface of Cr and to band degeneracies at the Fermi level that split at this transition. We have determined the magnetic groups of the transversely and longitudinally modulated spin structure and give the corepresentations to which the commensurate, the transverse, and the longitudinal spin-density-wave states belong. It turns out that, in contrast to the longitudinal, the transverse spin-density wave is not quite incommensurate because its periodicity is an even multiple of the lattice constant. We speculate that this behavior might be responsible for the spin-flip transition at  $T_{sf}=123$  K. The special form of the resulting corepresentations shows that the two incommensurate states are accompanied by lattice distortions and that all three magnetic states are  $N$ -electron Bloch states with nonvanishing wave vector. While the commensurate and the transverse spin-density waves, because of their symmetry, are exactly antiferromagnetic, we cannot exclude the longitudinally modulated structure's being slightly ferromagnetic.

### I. INTRODUCTION

The essential approximation of the atomic or Heisenberg model is that the electrons responsible for magnetism are situated on the atoms. This rough approximation leads to a fundamental understanding of magnetism, although, as is well known, in most metals electrons belonging to partly filled energy bands are responsible for magnetism. In such bands the electrons may hop from one atom to another in performing their band motion, which is determined by both their translational energy and their Coulomb interaction.

The translational energy causes a finite time of stay  $\tau$  of the electrons on the atoms, which is connected with the bandwidth  $\Delta$  according to  $\tau \approx \hbar/\Delta$  and which in the transition metals is of order  $10^{-15}$  s. The question of why, despite this extremely small  $\tau$ , the electrons may have atomlike character is treated in great detail by Hubbard.<sup>1</sup> He argues that it is intra-atomic correlation effects in narrow bands that leads to the atomic behavior. In brief, the motion of all the electrons that occupy a localized orbital one after another is correlated in such a way that we can speak of localized electron states.

The influence of the Coulomb interaction on the electronic motion is difficult to estimate. A special part of the Coulomb interaction operator, which, in Sec. II, will be denoted by  $H_z$ , generates transitions between adjacent localized states. These transitions reduce the possibility of an atomic model since they further decrease the short time of stay  $\tau$  and destroy any correlated motion of the electrons. More quantitative statements on the influence

of  $H_z$  are difficult to make since this operator represents that part of the Coulomb interaction whose matrix elements depend crucially on the exact form of the basis functions and hence are most hardly calculated.

It is found experimentally that, e.g., the  $d$  electrons of the transition metals exhibit behavior of both the band and the atomic model.<sup>1</sup> Thus, the interaction  $H_z$  evidently does not destroy the atomlike character of these electrons. The reason for this ineffectiveness of  $H_z$  might be that this operator represents only a small perturbation. This argument seems to be born out by the special form of the matrix elements of  $H_z$  which vanish if "sufficiently localized" Wannier functions are used as basis functions. Such Wannier functions, however, do not exist. In particular, the Wannier functions of the narrowest partly filled bands of the metals extend far beyond the Wigner-Seitz cell. If, nevertheless, the basis functions are assumed to be approximately that localized that  $H_z$  vanishes, then the exchange term  $H_{ex}$  of the Coulomb operator vanishes, too, and all exchange effects are discarded from the beginning.

The nonadiabatic Heisenberg model as proposed recently by the author<sup>2</sup> treats the operator  $H_z$  in a new way. As explained in Sec. II (and, in detail, in Ref. 2)  $H_z$  is *not* assumed to be so small that it is ineffective in partly filled bands but a nonadiabatic mechanism is postulated which makes  $H_z$  ineffective in narrow bands. We show (in Sec. II) that the assumptions of this model are a generalization of the assumptions made in the original Heisenberg theory of magnetism. The essence of the new group-theoretical model is that the question as to which

TABLE I. Matrix representatives of four special irreducible corepresentations (which only differ by unessential factors  $d_1 = \pm 1$  and  $d_2 = \pm 1$ ) of the group  $G^T$  as given in Eq. (A5). The perfect antiferromagnetic state  $|G^n\rangle$  of Cr and the related time-inverted state are basis vectors of one of these corepresentations. These matrices cannot be unitarily transformed because only the basis functions of the given matrices satisfy the Pauli principle within the nonadiabatic system. The last column shows that  $|G^n\rangle$  is an  $N$ -electron Bloch state with wave vector  $\mathbf{k}_M$ , the vector of the point  $M$  in the antiferromagnetic Brillouin zone (as given, e.g., in Fig. 3 of Ref. 11).

$\{C_{2x} \tau\}$	$\{C_{4z}^+ 0\}$	$\{\sigma_z 0\}$	$\{I 0\}$	$\{K \tau\}$	$\begin{matrix} \{E \tau\} \\ \{K 0\} \end{matrix}$	$\{E \mathbf{R}\}$
$\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}$	$\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} d_1$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} d_2$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} d_2$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} e^{-i\mathbf{k}_M \cdot \mathbf{R}}$

exchange effects are possible in a given metal, depends on the special symmetry of the Wannier functions of the narrowest, roughly half-filled energy bands of this metal.

The nonadiabatic Heisenberg model has first been applied to superconductivity. Here the fact was used that spin-dependent Wannier functions with a special symmetry can be constructed from the Bloch functions of a distinct narrow, roughly half-filled band (called the  $\sigma$  band) of the superconductors. The symmetry and spin dependence of these functions suggest that, contrary to common belief, a new exchange effect, namely spin-phonon interaction, is responsible for superconductivity.<sup>2</sup> This statement does not contradict but extends the BCS and Eliashberg theory of superconductivity<sup>3</sup> and may help to understand the high transition temperature of the new superconductors within the BCS theory.<sup>4</sup>

In this paper, the nonadiabatic Heisenberg model is ap-

plied to the itinerant antiferromagnetism in Cr. Here, it is applicable because the band structure of Cr exhibits a characteristic feature: The Bloch functions of one of the narrowest, roughly half-filled bands of this transition metal can be transformed into an orthonormal set of optimally localizable Wannier functions which are symmetry-adapted to the space group  $D_{4h}^6$  of the perfect antiferromagnetic structure.<sup>5</sup> This "antiferromagnetic band" (AF band, see Fig. 1 of Ref. 5) is obviously connected with the stability of the spin-density-wave state in Cr because the other nonferromagnetic bcc transition metals (except for Mo), V, Nb, W, and Ta, do not possess such an AF band (or have an AF band which is far from being half filled).<sup>5</sup>

Starting from the symmetry of the AF-band Wannier functions we show in Sec. III A that, within the nonadiabatic Heisenberg model, the AF-band electrons may

TABLE II. Matrix representatives belonging to two special irreducible corepresentations (with  $d = \pm 1$ ) of the magnetic groups  $G_x^i + \{K|0\}G_x^i$  and  $G_z^i + \{K|0\}G_z^i$  as given by Eqs. (4.6) and (4.13), respectively. As in Table I the given matrices cannot be unitarily transformed. Top: The transverse spin-density-wave state  $|G_x^{ni}\rangle$  and the related time-inverted state are basis vectors of one of these two corepresentations. The first column shows that the operation  $\{C_{2x}|\tau_x\}$  cannot be taken out of  $G_x^i$  because, otherwise, the corepresentations become reducible and, hence,  $|G_x^{ni}\rangle$  gets unstable (see Sec. IV). The third column shows that the nonadiabatic Hamiltonian  $H_x^{ni}$  [see Eq. (4.2)] has real eigenvalues and, according to the last column,  $|G_x^{ni}\rangle$  is an  $N$ -electron Bloch state with the wave vector  $\hat{Q}$  of one of the points on the surface of the Brillouin zone as given by Eq. (4.9).  $\hat{\mathbf{R}}$  denotes a primitive translation of  $G_x^i$ . Bottom: The longitudinal spin-density-wave state  $|G_z^{ni}\rangle$  and the related time-inverted state are basis vectors of one of these two corepresentations. These corepresentations are irreducible although no symmetry operation of  $G_z^i$  is associated with a nonprimitive translation and, therefore, the state  $|G_z^{ni}\rangle$  is, in contrast to  $|G_x^{ni}\rangle$ , totally incommensurate with the lattice constant. The third column shows again that the nonadiabatic Hamiltonian  $H_z^{ni}$  has real eigenvalues and, according to the last column,  $|G_z^{ni}\rangle$  has the crystal momentum  $\hat{Q}$  which is given by one of the vectors in Eq. (4.16).  $\hat{\mathbf{R}}$  denotes a primitive translation of  $G_z^i$ .

$\{C_{2x} \tau_x\}$	$\{\sigma_z 0\}$	$\{KI \tau_x\}^a$	$\begin{matrix} \{I \tau_x\}^a \\ \{K 0\} \end{matrix}$	$\{E \hat{\mathbf{R}}\}$
$\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} d$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} e^{-i\hat{Q} \cdot \hat{\mathbf{R}}}$
$\{C_{4z}^+ 0\}$	$\{I 0\}$	$\{K\sigma_x 0\}$	$\begin{matrix} \{\sigma_x 0\} \\ \{K 0\} \end{matrix}$	$\{E \hat{\mathbf{R}}\}$
$\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} d$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} e^{-i\hat{Q} \cdot \hat{\mathbf{R}}}$

<sup>a</sup> The nonprimitive translation  $\tau_x$  associated with  $KI$  and  $I$  is omitted when the origin of the coordinate system in Fig. 2 lies at point  $I_0$ .

lower their Coulomb energy by forming a state which possesses a spin structure with the space group  $D_{4h}^6$ . In this context we need no new assumptions going beyond those already made in Ref. 2 and listed in Sec. II of this paper. This result suggests that the special symmetry of the AF band is responsible for the stability of the spin-density-wave state in Cr and it corroborates the assumptions of the nonadiabatic Heisenberg model and hence the foregoing statement on superconductivity.

According to a group-theoretical theorem the eigenstates of any Hamiltonian  $H$  are basis vectors of an irreducible representation of the space group of  $H$ . Assuming that this theorem is also applicable to magnetic states, i.e., to magnetic groups and their corepresentations, we determine in Sec. III C the corepresentation of the magnetic group of Cr to which the perfect antiferromagnetic state belongs and give it in Table I. A result is that this state is an  $N$ -electron Bloch state with wave vector  $\mathbf{k}_M$ , the vector of the point  $M$  in the Brillouin zone of antiferromagnetic Cr. This result is in agreement with the concept of a static spin-density wave with nonvanishing wave vector as it was proposed by Overhauser.<sup>6</sup> The wave vector  $\mathbf{k}_M$ , however, is not a vector of the antiferromagnetic reciprocal lattice and therefore it is not identical with the vector  $\mathbf{Q}$  observed in neutron-diffraction experiments.

The commensurate-incommensurate transition is not caused by the interaction  $H_z$ , i.e., by correlation energy. It is ascribed, in the usual way, to the peculiar geometric features of the Fermi surface of Cr (Ref. 7) and, as shown in Sec. V F, to the special symmetry of the related Bloch functions. Starting again from the above-mentioned assumption, we determine in Sec. IV the magnetic groups of the two incommensurate spin structures, i.e., of the transversely and longitudinally modulated structure, and the corepresentations to which the related spin-density-wave states belong (see Table II). It turns out that the transverse, in contrast to the longitudinal, spin-density wave is not quite incommensurate with the lattice constant (see Sec. IV A). We speculate (in Sec. V G) that this fact might be responsible for the spin-flip transition observed at the temperature  $T_{sf} = 123$  K.

In the Appendixes we describe the magnetic group of perfect antiferromagnetic Cr and give the symmetry properties of the optimally localizable Wannier functions of the AF band as far as they are needed in the present paper.

## II. NONADIABATIC HEISENBERG MODEL

In this section we present the nonadiabatic Heisenberg model as introduced in a former paper<sup>2</sup> by giving the assumptions defining this new group-theoretical model. Further, we show that it is a generalization of the original Heisenberg model<sup>8</sup> of magnetism.

Let be

$$H = H_{\text{HF}} + H_{\text{Cb}} \quad (2.1)$$

the Hamiltonian of the electrons of a given roughly half-filled energy band, say, of the AF band of Cr denoted in Fig. 1 of Ref. 5 by the heavy line, with

$$H_{\text{HF}} = \sum_{\mathbf{T}, \mathbf{T}', s} \langle \mathbf{T} | H_{\text{HF}} | \mathbf{T}' \rangle c_{\mathbf{T}s}^\dagger c_{\mathbf{T}'s} \quad (2.2)$$

and

$$H_{\text{Cb}} = \sum_{T, s} \langle \mathbf{T}_1, \mathbf{T}_2 | H_{\text{Cb}} | \mathbf{T}'_1, \mathbf{T}'_2 \rangle c_{\mathbf{T}_1 s}^\dagger c_{\mathbf{T}_2 s}^\dagger c_{\mathbf{T}'_2 s} c_{\mathbf{T}'_1 s} \quad (2.3)$$

representing the Hartree-Fock and the Coulomb energy, respectively. Other contributions to  $H$  from the electrons not belonging to the considered band are neglected even as spin-orbit effects. A further operator subtracting that part of  $H_{\text{Cb}}$  which is already included in  $H_{\text{HF}}$  does not matter in the following and is suppressed for brevity.

The matrix elements of  $H_{\text{Cb}}$ ,

$$\begin{aligned} & \langle \mathbf{T}_1, \mathbf{T}_2 | H_{\text{Cb}} | \mathbf{T}'_1, \mathbf{T}'_2 \rangle \\ &= \frac{e^2}{2} \int \frac{\langle \mathbf{T}_1 | \mathbf{r} \rangle \langle \mathbf{T}_2 | \mathbf{r}' \rangle \langle \mathbf{r}' | \mathbf{T}'_2 \rangle \langle \mathbf{r} | \mathbf{T}'_1 \rangle}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' , \end{aligned} \quad (2.4)$$

are integrals over Wannier functions forming a complete basis in the considered band, say, the functions given in Eq. (B2). The fermion operators  $c_{\mathbf{T}s}^\dagger$  and  $c_{\mathbf{T}s}$  create and annihilate, respectively, electrons with spin  $s$  in the localized states  $|\mathbf{T}, s\rangle$ .

Using the same arguments as in Sec. II of Ref. 2 we split  $H_{\text{Cb}}$  into three parts,

$$H_{\text{Cb}} = H_c + H_{\text{ex}} + H_z , \quad (2.5)$$

with the operator of Coulomb repulsion  $H_c$  containing all the matrix elements of  $H_{\text{Cb}}$  with  $\mathbf{T}_1 = \mathbf{T}'_1$  and  $\mathbf{T}_2 = \mathbf{T}'_2$ , the exchange operator  $H_{\text{ex}}$  containing the matrix elements with  $\mathbf{T}_1 = \mathbf{T}'_2$  and  $\mathbf{T}_2 = \mathbf{T}'_1$ , and  $H_z$  comprising the remaining matrix elements, i.e., the matrix elements with

$$\{\mathbf{T}_1, \mathbf{T}_2\} \neq \{\mathbf{T}'_1, \mathbf{T}'_2\} \quad (2.6)$$

where  $\{\mathbf{T}_1, \mathbf{T}_2\} = \{\mathbf{T}'_1, \mathbf{T}'_2\}$  means  $\mathbf{T}_1 = \mathbf{T}'_1$  and  $\mathbf{T}_2 = \mathbf{T}'_2$  or  $\mathbf{T}_1 = \mathbf{T}'_2$  and  $\mathbf{T}_2 = \mathbf{T}'_1$ .

The first assumption of the nonadiabatic Heisenberg model reads: If the considered band (like the AF band) is one of the narrowest, roughly half-filled bands of the given metal, then

$$\langle G | H | G \rangle > \langle G' | H' | G' \rangle , \quad (2.7)$$

where  $|G\rangle$  and  $|G'\rangle$  are the *exact* ground states of  $H$  and

$$H' = H_{\text{HF}} + H_c + H_{\text{ex}} = H - H_z , \quad (2.8)$$

respectively. Relation (2.7), which is substantiated in Sec. II of Ref. 2, says that the energy of the electrons increases by

$$\Delta E = \langle G | H | G \rangle - \langle G' | H' | G' \rangle \quad (2.9)$$

when the interaction  $H_z$  is switched on. Shortly, that means that in *narrow* bands a *dual*, bandlike *and* atomic, character of the conduction electrons is *energetically* more favorable than a pure bandlike character.

With the aim to find a mechanism making  $H_z$

ineffective, the adiabatic localized functions  $\langle \mathbf{r}, t | \mathbf{T}, s \rangle$  [cf. Eq. (B9)] are replaced by nonadiabatic localized functions

$$\langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}, m, \nu \rangle, \quad (2.10)$$

where the new coordinate  $\mathbf{q}$  describes that part of the motion of the nuclei which nonadiabatically follows the motion of the electron occupying the state  $|\mathbf{T}, m, \nu\rangle$ . With free atoms, this nonadiabatic motion of the nuclei (which is experimentally well established by the isotope shift of the spectral lines) occurs in such a way that the total atomic center of mass stays at rest. In a solid state, consisting of bound atoms, this restriction does not hold, and hence the localized centers of mass may take different states of motion labeled by the new quantum number  $\nu$ .

The quantum number of the "crystal spin"  $m = \pm \frac{1}{2}$  replaces the spin quantum number  $s$  in the nonadiabatic system. It is related to the point group operators of the crystal in the same way as  $s$  is related to the symmetry

operators  $S(\alpha)$  of the three-dimensional rotation group  $O(3)$  (see Sec. III of Ref. 2) and, consequently, the effect of the time-inversion operator is

$$P^n(\{K|0\}) \langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}, m, \nu \rangle = g_m(K) \langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}, -m, \nu \rangle, \quad (2.11)$$

where  $P^n(\{K|0\})$  and  $g_m(K)$  are given in Eq. (3.6) (for  $\tau=0$ ) and Eq. (B14), respectively.

The second assumption of the nonadiabatic Heisenberg model states that, if relation (2.7) is true, the nonadiabatic motion of the nuclei occurs in such a way that the matrix elements of  $H_z$  vanish,

$$\langle \mathbf{T}_1, m_1; \mathbf{T}_2, m_2 | H_{\text{Cb}}^n | \mathbf{T}'_1, m'_1; \mathbf{T}'_2, m'_2 \rangle = 0 \quad (2.12)$$

for

$$\{\mathbf{T}_1, \mathbf{T}_2\} \neq \{\mathbf{T}'_1, \mathbf{T}'_2\},$$

where

$$\begin{aligned} & \langle \mathbf{T}_1, m_1; \mathbf{T}_2, m_2 | H_{\text{Cb}}^n | \mathbf{T}'_1, m'_1; \mathbf{T}'_2, m'_2 \rangle \\ &= \frac{e^2}{2} \sum_{i, i'} \int \frac{\langle \mathbf{T}_1, m_1, n | \mathbf{r}, t, \mathbf{q} \rangle \langle \mathbf{T}_2, m_2, n | \mathbf{r}', t', \mathbf{q}' \rangle \langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}'_1, m'_1, n \rangle \langle \mathbf{r}', t', \mathbf{q}' | \mathbf{T}'_2, m'_2, n \rangle}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' d\mathbf{q} d\mathbf{q}'. \end{aligned} \quad (2.13)$$

Equation (2.12) is suggested by the basic idea that only small changes of the electronic orbitals are required to prevent (at least partially) the increase of the energy by  $\Delta E$  [as given in Eq. (2.9)] since the interaction  $H_z$  depends crucially on the exact form of the Wannier functions (see Sec. II of Ref. 2). This modified electronic motion is accompanied by a nonadiabatic motion of the nuclei because, within the adiabatic approximation, Eq. (2.7) is true. The quantum number  $\nu$ , for which Eq. (2.12) is true, is denoted, in Eq. (2.13), by  $n$ .

The operator of Coulomb interaction in the nonadiabatic system now can be written as

$$\begin{aligned} H_{\text{Cb}}^n &= \sum_{\mathbf{T}, m} \langle \mathbf{T}_1, m_1; \mathbf{T}_2, m_2 | H_{\text{Cb}}^n | \mathbf{T}'_1, m'_1; \mathbf{T}'_2, m'_2 \rangle \\ &\quad \times c_{\mathbf{T}'_1, m'_1}^{\dagger} c_{\mathbf{T}'_2, m'_2}^{\dagger} c_{\mathbf{T}_2, m_2}^n c_{\mathbf{T}_1, m_1}^n, \end{aligned} \quad (2.14)$$

where

$$\{\mathbf{T}_1, \mathbf{T}_2\} = \{\mathbf{T}'_1, \mathbf{T}'_2\}. \quad (2.15)$$

The new fermion operators  $c_{\mathbf{T}'_m}^{\dagger}$  and  $c_{\mathbf{T}'_m}^n$  create and annihilate, respectively, an electron in the nonadiabatic state  $|\mathbf{T}, m, n\rangle$ . They obey (for fixed  $n$ ) the commutation rules of fermion operators since  $H_{\text{Cb}}^n$  must be invariant with respect to the permutation of two localized states. Consequently, the nonadiabatic localized functions are, for fixed  $n$ , orthogonal according to

$$\sum_i \langle \mathbf{T}', m', n | \mathbf{r}, t, \mathbf{q} \rangle \langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}, m, n \rangle d\mathbf{r} d\mathbf{q} = \delta_{\mathbf{T}'\mathbf{T}} \delta_{m'm}, \quad (2.16)$$

where the integration runs over both  $\mathbf{r}$  and  $\mathbf{q}$ . In the

nonadiabatic system, the naked electrons hence do not have exactly Fermi character. Here, the Fermi excitations are represented by electrons occupying the states  $|\mathbf{T}, m, n\rangle$ , i.e., by electrons carrying with them some nonadiabatic motion of the nuclei.

The effect of  $H_z$  can be interpreted as follows. If we put  $H_z=0$ , the ground state of the electron system is represented by the ground state  $|G'\rangle$  of  $H'$  [see Eq. (2.8)]. When  $H_z$  is switched on, the electrons couple to the motion of the nuclei in such a way that the increase of energy by  $\Delta E$  [see Eq. (2.9)] is prevented. Since  $H_z$  is a small operator, we may assume that during the activation of  $H_z$  the symmetry of the ground state stays unchanged. The third (and last) assumption of the nonadiabatic Heisenberg model hence states that  $H_{\text{Cb}}^n$  has, with respect to the space-group operators, the same commutation properties as

$$H'_{\text{Cb}} = H_c + H_{\text{ex}} = H_{\text{Cb}} - H_z. \quad (2.17)$$

The energy

$$E^n = \langle G^n | H^n | G^n \rangle \quad (2.18)$$

of the ground state of the nonadiabatic operator

$$H^n = H_{\text{HF}} + H_{\text{Cb}}^n \quad (2.19)$$

is given by

$$E^n = \langle G' | H' | G' \rangle \quad (2.20)$$

[with  $H'$  being defined in Eq. (2.8)] if we neglect the energy of the motion of the nuclei and the energy rise caused by the slight change of the electronic orbitals during the

activation of  $H_z$  [i.e., the true ground-state energy is slightly higher than the energy given in Eq. (2.20)]. Thus, by the transition from the adiabatic to the nonadiabatic system the electrons gain the energy  $\Delta E$  as given in Eq. (2.9).

We shall show in the next section that at the transition from the adiabatic to the nonadiabatic system the Hamiltonian becomes spin dependent. The energy gain at this transition,  $\Delta E$ , may be called "nonadiabatic exchange energy" because it has the same physical origin as the familiar exchange energy calculated by an exchange integral. This last statement shall be substantiated in the following.

Consider first the hydrogen molecule which may be regarded as a rudimentary antiferromagnet. The second assumption (2.12) of the nonadiabatic Heisenberg model, written for the hydrogen molecule, states that there are no transitions between the two hydrogen atoms. Hence, we get the basic assumption of the familiar Heitler-London treatment of the hydrogen molecule since at each atom we have exactly one electron.

Within the Heitler-London model, a state in which the two electrons are at the same hydrogen atom is ruled out by stating that such a state would have a markedly higher energy. This statement corresponds to the first assumption (2.7) of the nonadiabatic Heisenberg model. The only new idea of the nonadiabatic model is that a state with one electron at each atom requires a nonadiabatic motion of the two nuclei. Since this question is meaningless within the Heitler-London theory we may state that the basic assumptions of both the Heitler-London and the nonadiabatic Heisenberg model are equal in the case of the hydrogen molecule.

In his original theory of magnetism, Heisenberg<sup>8</sup> has transferred the Heitler-London model to the metals by assuming that there is exactly one electron at each atom of a metal. The basic assumption (2.12) of the nonadiabatic model differs slightly from this strong demand since, in systems which have (in contrast to the hydrogen molecule) translation symmetry, Eq. (2.12) does not lead to a state with one electron at each atom. Because of their translational energy, the electrons may occupy configurations with different numbers of electrons at the atoms. Therefore, we call the nonadiabatic model a generalization of the original Heisenberg model. Spin-dependent effects in both models have the same physical origin since models with equivalent assumptions are equivalent.

### III. THE PERFECT ANTIFERROMAGNETIC STATE OF CHROMIUM

#### A. Itinerant antiferromagnetism

In this section the nonadiabatic Heisenberg model as presented in the preceding section is applied to chromium. That means, the Wannier functions  $\langle \mathbf{r} | \mathbf{T} \rangle$  in Eq. (2.4) now are identified with the functions  $\langle \mathbf{r} | \mathbf{T} \rangle$  given in Eq. (B2). These functions form a complete basis within the AF band denoted in Fig. 1 of Ref. 5 by the heavy line and have the symmetry given in Eqs. (B3)–(B8). From

these symmetry properties of the basis functions and the assumptions of the nonadiabatic Heisenberg model we shall conclude that the nonadiabatic ground state of the AF-band electrons possesses a spin structure with the space group  $D_{4h}^6$  of perfect antiferromagnetic Cr.

Equations (B3)–(B5) show that the adiabatic operator  $H'_{Cb}$  [see Eq. (2.17)] commutes with the symmetry operators  $P(a)$  [as given in Eqs. (A10) and (A11)] of the magnetic group  $G^M$  of perfect antiferromagnetic Cr,

$$[H'_{Cb}, P(a)] = 0 \quad \text{for } a \in G^M. \quad (3.1)$$

Therefore, according to the third assumption of the nonadiabatic Heisenberg model, also the nonadiabatic Coulomb interaction  $H_{Cb}^n$  commutes with the symmetry operators  $P^n(a)$  belonging to  $G^M$  in the nonadiabatic system,

$$[H_{Cb}^n, P^n(a)] = 0 \quad \text{for } a \in G^M. \quad (3.2)$$

The nonadiabatic localized functions hence have the same symmetry properties as the Wannier functions given in Eq. (B9), i.e.,

$$P^n(\{\alpha | \mathbf{t}\}) \langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}, m, n \rangle = d(\alpha) g_m(\alpha) \langle \mathbf{r}, t, \mathbf{q} | \alpha \mathbf{T} + \mathbf{t}, \alpha m, n \rangle \quad (3.3)$$

for

$$\{\alpha | \mathbf{t}\} \in D_{4h}^6$$

and

$$P^n(\{K | \tau\}) \langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}, m, n \rangle = g_m(K) \langle \mathbf{r}, t, \mathbf{q} | \mathbf{T} + \tau, -m, n \rangle, \quad (3.4)$$

where the nonadiabatic symmetry operators

$$P^n(\{\alpha | \mathbf{t}\}) = P(\{\alpha | \mathbf{t}\}) Q(\alpha) S(\alpha) \quad (3.5)$$

and

$$P^n(\{K | \tau\}) = P(\{K | \tau\}) S(K) \quad (3.6)$$

now act on  $\mathbf{r}$ ,  $t$ , and  $\mathbf{q}$ :  $P(\{\alpha | \mathbf{t}\})$  acts on  $\mathbf{r}$  as given in Eq. (A10),  $Q(\alpha)$  acts on  $\mathbf{q}$  according to

$$Q(\alpha) f(\mathbf{q}) = f(\alpha^{-1} \mathbf{q}), \quad (3.7)$$

and  $S(\alpha)$  acts on  $t$  as given in Eq. (B11). The time-inversion operator  $P(\{K | \tau\})$  acts on  $\mathbf{r}$  and  $\mathbf{q}$  according to

$$P(\{K | \tau\}) f(\mathbf{r}, \mathbf{q}) = f^*(\mathbf{r} - \tau, \mathbf{q}) \quad (3.8)$$

and  $S(K)$  acts on  $t$  as given in Eq. (B13). The  $c$  numbers  $g_m(\alpha)$  and  $g_m(K)$  are equal to  $g_s(\alpha)$  [see Eq. (B15)] and  $g_s(K)$  [see Eq. (B14)], respectively, for  $m = s$ , and  $\alpha m$  is defined in Eq. (B16) for  $m = s$ . The numbers  $d(\alpha) = \pm 1$  form a one-dimensional representation of  $D_{4h}$ .

The quantum number  $n$  labels the nonadiabatic localized functions for which Eq. (2.12) is valid. In principle,  $n$  may depend on  $m$  and  $T$ ,

$$n \equiv n(m, T). \quad (3.9)$$

Equation (3.2) shows that  $n$  may take two different values  $n_1$  and  $n_2$ ,

$$n = \begin{cases} n_1 & \text{for } \mathbf{T}=\mathbf{R} \text{ and } m = \frac{1}{2} \\ n_1 & \text{for } \mathbf{T}=\mathbf{R}+\boldsymbol{\tau} \text{ and } m = -\frac{1}{2} \\ n_2 & \text{for } \mathbf{T}=\mathbf{R}+\boldsymbol{\tau} \text{ and } m = \frac{1}{2} \\ n_2 & \text{for } \mathbf{T}=\mathbf{R} \text{ and } m = -\frac{1}{2}, \end{cases} \quad (3.10)$$

because, according to Eqs. (3.3) and (3.4), the operators  $P^n(a)$  do not transform the functions labeled by  $n_1$  into the functions labeled by  $n_2$  (and vice versa). We now show that  $n_1$  and  $n_2$  are different.

The important Eqs. (B6) and (B8) show immediately that the operator  $H'_{\text{Cb}}$  [see Eq. (2.17)] does not commute with the time-inversion operator,

$$[H'_{\text{Cb}}, P(\{K|0\})] \neq 0, \quad (3.11)$$

since the operator

$$P(\{K|0\})H'_{\text{Cb}}P(\{K|0\})^{-1}$$

has matrix elements violating the condition

$$\{T_1, T_2\} = \{T'_1, T'_2\}.$$

The third assumption of the nonadiabatic Heisenberg model states that therefore also the nonadiabatic Coulomb operator  $H^n_{\text{Cb}}$  does not commute with the time-inversion operator,

$$[H^n_{\text{Cb}}, P^n(\{K|0\})] \neq 0. \quad (3.12)$$

Assume that the nonadiabatic localized function

$$\langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}_1, m_1, n_1 \rangle$$

belongs to the set of functions satisfying Eq. (2.12), i.e., that  $\mathbf{T}_1$  and  $m_1$  have the form given in the first or second row of Eq. (3.10). Relation (3.12) is true if and only if the function

$$P^n(\{K|0\})\langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}_1, m_1, n_1 \rangle = g_{m_1}(K)\langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}_1, -m_1, n_1 \rangle \quad (3.13)$$

[see Eq. (2.11)] does not also belong to this set of functions. Therefore, relation (3.12) gives

$$n_1 \neq n_2 \quad (3.14)$$

since, according to Eq. (3.10), the nonadiabatic function

$$\langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}_1, -m_1, n_2 \rangle$$

belongs to the functions satisfying Eq. (2.12).

Relation (3.14) shows that

$$\langle \mathbf{r}, t, \mathbf{q} | \mathbf{T}, m, n \rangle \neq \langle \mathbf{r}, \mathbf{q} | \mathbf{T}, n \rangle \langle t | m \rangle,$$

i.e., the nonadiabatic localized functions satisfying Eq. (2.12) cannot be written as products of two functions depending on  $\mathbf{r}$  and  $\mathbf{q}$  and on  $t$ , respectively, since, at a fixed lattice point  $\mathbf{T}$ , the quantum number  $n$  depends on  $m$ . Therefore, the nonadiabatic Coulomb operator  $H^n_{\text{Cb}}$  does not commute with that part  $S(K)$  of the time-inversion operator acting only on the spin coordinates,

$$[H^n_{\text{Cb}}, S(K)] \neq 0, \quad (3.15)$$

so that

$$S(K)|G^n\rangle \neq |G^n\rangle \quad (3.16)$$

[with  $S(K)$  being given in Eq. (B12)].

This last relation shows that the nonadiabatic ground state  $|G^n\rangle$  of  $H^n$  possesses a spin structure which, according to Eq. (3.2), has the antiferromagnetic group  $G^M$ . This is the result of this section.

Relation (3.15) is characteristic for the nonadiabatic system because the adiabatic operator  $H'_{\text{Cb}}$  commutes with  $S(K)$ ,

$$[H'_{\text{Cb}}, S(K)] = 0, \quad (3.17)$$

since  $H'_{\text{Cb}}$  does not depend on the spin coordinates. The magnetic order in  $|G^n\rangle$  is caused by the nonadiabatic mechanism which, according to Eq. (2.12), makes the interaction  $H_z$  ineffective. The stabilization energy of the magnetic ordered state, i.e., the energy difference between the paramagnetic and the perfect antiferromagnetic state, is the nonadiabatic exchange energy  $\Delta E$  given in Eq. (2.9).

The adiabatic and nonadiabatic Hamiltonians  $H$  and  $H^n$  represent the energy of the electrons belonging to the *partly-filled* AF band of Cr. Thus, relation (3.15) is not connected with the existence of any localized moments at the Cr atoms. The spin structure in  $|G^n\rangle$  can therefore be interpreted in terms of itinerant antiferromagnetism.

## B. Spin-phonon interaction

The operator  $H^n_{\text{Cb}}$  as given in Eq. (2.14) has nonvanishing matrix elements with

$$\{m_1, m_2\} \neq \{m'_1, m'_2\}$$

contradicting the conservation of angular momentum within the nonadiabatic system. As explained in detail in Sec. IV of Ref. 2, this violation forces the electron spins to couple to the phonons. In the present paper, this spin-phonon interaction is ignored since we give only symmetry arguments which are independent of whether or not the considered states are purely electronic. For complete understanding of the (constraining) forces which keep the spins antiparallel in  $|G^n\rangle$  the spin-phonon interaction has to be included.

## C. Spin-density-wave state

In this section we show that evidently the nonadiabatic ground state  $|G^n\rangle$  of perfect antiferromagnetic Cr and the time-inverted state

$$|\bar{G}^n\rangle = P^n(\{K|0\})|G^n\rangle \quad (3.18)$$

are basis vectors of an *irreducible* corepresentation of the group

$$G^T = G^M + \{K|0\}G^M \quad (3.19)$$

[as given in Eq. (A5)]. Under this assumption we derive the four possible corepresentations (which only differ by unessential factors) given in Table I to which  $|G^n\rangle$  and  $|\bar{G}^n\rangle$  can belong.

From Eq. (3.2) we obtain

$$P^n(a)|G^n\rangle = c(a)|G^n\rangle \quad \text{for } a \in G^M \quad (3.20)$$

with the  $c$  numbers  $c(a)$  forming a one-dimensional corepresentation of  $G^M$ , and Eq. (3.12) gives

$$|\bar{G}^n\rangle \neq |G^n\rangle \quad (3.21)$$

[see Eq. (3.18)]. The state  $|\bar{G}^n\rangle$  is the ground state of the operator

$$\bar{H}^n = P^n(\{K|0\rangle\})H^nP^n(\{K|0\rangle\})^{-1} \quad (3.22)$$

which, according to Eq. (3.12), differs from  $H^n$ . Both operators have the same ground-state energy  $E^n$ ,

$$H^n|G^n\rangle = E^n|G^n\rangle \quad (3.23)$$

and

$$\bar{H}^n|\bar{G}^n\rangle = E^n|\bar{G}^n\rangle, \quad (3.24)$$

because  $E^n$  is real [since  $H^n$  commutes, according to Eq. (3.2), with the antiunitary operator  $P^n(\{K|\tau\})$ ].

The operator  $H^n$  may be written as

$$H^n = F^n \tilde{H} F^n \quad (3.25)$$

where the projection operator

$$F^n = \frac{1}{N} \sum_{T,m} c_{Tm}^{n\dagger} c_{Tm}^n \quad (3.26)$$

projects on the space  $A^n$  being spanned by wave functions of the form

$$|\phi_i^n\rangle = c_{T_1 m_1}^{n\dagger} c_{T_2 m_2}^{n\dagger} \cdots c_{T_N m_N}^{n\dagger} |0\rangle \quad (3.27)$$

and

$$\tilde{H} = -\frac{\hbar^2}{2m} \frac{d^2}{d\mathbf{r}^2} + V(\mathbf{r}) + \frac{1}{2} \sum_{\substack{\mu,\nu \\ \mu \neq \nu}} \frac{e^2}{|\mathbf{r}_\mu - \mathbf{r}_\nu|} \quad (3.28)$$

is the familiar electronic Hamiltonian [with  $V(\mathbf{r})$  being the potential of the nuclei and the core electrons].  $N$  is the number of electrons of the AF band.

The time-inverted operator  $\bar{H}^n$  as given in Eq. (3.22) also can be written in the form

$$\bar{H}^n = \bar{F}^n \tilde{H} \bar{F}^n, \quad (3.29)$$

where

$$\bar{F}^n = P^n(\{K|0\rangle\})F^nP^n(\{K|0\rangle\})^{-1}, \quad (3.30)$$

since  $\tilde{H}$  commutes with the time-inversion operator,

$$[\tilde{H}, P^n(\{K|0\rangle\})] = 0. \quad (3.31)$$

Equations (3.31) and (3.12) immediately show that the projection operator  $F^n$  (as well as  $\bar{F}^n$ ) does not commute with the time-inversion operator,

$$[F^n, P^n(\{K|0\rangle\})] \neq 0. \quad (3.32)$$

Thus,  $F^n$  and  $\bar{F}^n$  project on different spaces  $A^n$  and  $\bar{A}^n$  which are physically equivalent. That means, the electron system may occupy either  $|G^n\rangle$  or  $|\bar{G}^n\rangle$ , but not a linear combination of these states because only the eigen-

states of  $F^n$  or  $\bar{F}^n$  satisfy the Pauli principle *within the nonadiabatic system*.

The projection operators  $F^n$  and  $\bar{F}^n$  commute with any observable, in particular with  $\tilde{H}$ ,

$$[\tilde{H}, F^n] = 0 \quad (3.33)$$

and

$$[\tilde{H}, \bar{F}^n] = 0, \quad (3.34)$$

since they project on the spaces  $A^n$  and  $\bar{A}^n$ , respectively, of the wave functions satisfying the Pauli principle in the nonadiabatic system. From Eqs. (3.23) and (3.24) we hence may derive the important equations

$$\tilde{H}|G^n\rangle = E^n|G^n\rangle \quad (3.35)$$

and

$$\tilde{H}|\bar{G}^n\rangle = E^n|\bar{G}^n\rangle, \quad (3.36)$$

showing that  $|G^n\rangle$  and  $|\bar{G}^n\rangle$  are eigenstates of  $\tilde{H}$  with the same eigenvalue  $E^n$ .

We now have written all the equations needed to determine the symmetry properties of  $|G^n\rangle$  and  $|\bar{G}^n\rangle$ . First Eq. (3.21) shows that these states are basis functions of a two-dimensional corepresentation, say  $R^T$ , of the group  $G^T$  as given in Eq. (3.19). This corepresentation we assume to be *irreducible* because both states [which are connected by Eq. (3.18)] are degenerate eigenstates of the same operator  $\tilde{H}$  which commutes, according to Eq. (3.31), with the time-inversion operator. Finally, Eq. (3.20) shows that  $|G^n\rangle$  alone belongs to a one-dimensional corepresentation of  $G^M$ . The assumption that  $R^T$  is irreducible is essential in what follows and, therefore, shall be substantiated for the present case.

If the states  $|G^n\rangle$  and  $|\bar{G}^n\rangle$  belong to a reducible corepresentation  $R^T$  of  $G^T$  then they can be unitarily transformed into states  $|G_1\rangle$  and  $|G_2\rangle$  belonging to a one-dimensional corepresentation of  $G^T$ . Since  $\tilde{H}$  is a linear operator,  $|G_1\rangle$  and  $|G_2\rangle$  are also eigenstates of  $\tilde{H}$  with the eigenvalues  $E_1$  and  $E_2$  (though neither  $|G_1\rangle$  nor  $|G_2\rangle$  satisfies the Pauli principle since they are not eigenstates of  $F^n$  or  $\bar{F}^n$ ). The coinciding values  $E_1$  and  $E_2$  may split when a small perturbation  $U$  is activated even if this  $U$  commutes with the time-inversion operator. The states  $|G_1\rangle$  and  $|G_2\rangle$ , but *not* the states  $|G^n\rangle$  and  $|\bar{G}^n\rangle$ , are, within first-order perturbation theory, eigenstates of the new operator  $\tilde{H} + U$ . Thus, if  $R^T$  were reducible, the states  $|G^n\rangle$  and  $|\bar{G}^n\rangle$  would become unstable if any small perturbation is activated and, therefore,  $R^T$  is assumed to be irreducible.

There are only the four corepresentations  $R^T$  given in Table I which satisfy all the above-mentioned conditions. These corepresentations can be determined<sup>9</sup> following the theory of corepresentations as given in Sec. 7.3. of the book of Bradley and Cracknell<sup>10</sup> and using Table II of Ref. 11.

The most interesting result is that all the  $R^T$  are derived from the eight one-dimensional representations of  $D_{4h}^6$  belonging to the point  $M$  in the Brillouin zone of antiferromagnetic Cr [see Fig. 1 and Table II of Ref. 11]. Hence we have

$$P^n(\{E|\mathbf{R}\})|G^n\rangle = e^{-ik_M \cdot \mathbf{R}}|G^n\rangle. \quad (3.37)$$

This equation shows that  $|G^n\rangle$  represents an  $N$ -electron Bloch state with the wave vector

$$\hat{\mathbf{Q}} = \mathbf{k}_M. \quad (3.38)$$

of the point  $M$ . In the usual notation,  $\hat{\mathbf{Q}}$  can be written as

$$\hat{\mathbf{Q}} = (\frac{1}{2}, \frac{1}{2}, 0) \frac{2\pi}{c} \quad (3.39)$$

with  $c$  being the lattice constant. This result is in excellent accordance with the concept of a static spin-density wave of nonvanishing wave vector in Cr first proposed by Overhauser.<sup>6</sup>

According to Eqs. (3.5) and (3.6) the space-group operators  $P^n(a)$  act on the three coordinates  $\mathbf{r}$ ,  $\mathbf{q}$ , and  $t$  of the nonadiabatic localized functions. Therefore, the magnetic structure represented by  $|G^n\rangle$  is not a pure spin-density wave but the induced moments are of both spin and orbital origin and are accompanied by lattice distortions.

It should be noted that the vector  $\hat{\mathbf{Q}}$  cannot be directly observed by neutron-diffraction experiments since  $M$  is not a point of the reciprocal antiferromagnetic lattice. Therefore,  $\hat{\mathbf{Q}}$  is not related to the magnetic reflections observed in the perfect antiferromagnetic state.

#### IV. MAGNETIC GROUPS AND SYMMETRY OF THE INCOMMENSURATE SPIN STRUCTURES

The energy  $E^n$  of the nonadiabatic ground state  $|G^n\rangle$  is given by the ground-state energy of the operator

$$H' = H_{\text{HF}} + H'_{\text{Cb}}$$

as given in Eq. (2.8) [see Eq. (2.20)]. The Coulomb term,  $H'_{\text{Cb}}$ , commutes with the symmetry operators of the perfect antiferromagnetic structure [see Eq. (3.1)] since the Wannier functions of the AF band are symmetry adapted to the group  $D_{4h}^6$ . The Coulomb energy hence favors a perfectly antiferromagnetic ground state and the transition to the incommensurate state is effected by the Hartree-Fock term  $H_{\text{HF}}$ . This transition is ascribed, in the usual way, to the peculiar geometric features of the Fermi surface of Cr (Ref. 7) and, as shown in Sec. V F, to the special symmetry of the Bloch functions at the Fermi level.

Within the nonadiabatic Heisenberg model the commensurate-incommensurate transition is accompanied by a small change of the nonadiabatic localized states in such a way that the projection operator  $F^n$  given in Eq. (3.26) is replaced by a new operator  $F_j^{ni}$  which no longer commutes with the operators  $P^n(a)$  related to the magnetic group of the commensurate state. The new operator  $F_j^{ni}$  only satisfies the equation

$$[F_j^{ni}, P^n(a)] = 0 \quad \text{for } a \in G_j^i \quad (4.1)$$

where  $G_j^i$  is the magnetic group of the incommensurate spin structure and  $j=x$  or  $z$  labels the structure with transverse and longitudinal modulation, respectively. According to Eq. (3.25) the nonadiabatic Hamiltonian

now has the form

$$H_j^{ni} = F_j^{ni} \tilde{H} F_j^{ni} \quad (4.2)$$

with  $\tilde{H}$  being given in Eq. (3.28). The magnetic groups  $G_j^i$  (with  $j=x$  or  $z$ ) of the two incommensurate spin structures and the symmetry of the two incommensurate spin-density-wave states  $|G_j^{ni}\rangle$  can be determined starting from the following conditions.

(i) According to Eq. (4.1), the incommensurate ground state  $|G_j^{ni}\rangle$  ( $j=x$  or  $z$ ) belongs to a *one-dimensional* corepresentation of the related group  $G_j^i$ .

(ii) As in Sec. III C the state  $|G_j^{ni}\rangle$  and its time-inverted state

$$|\bar{G}_j^{ni}\rangle = P^n(\{K|0\})|G_j^{ni}\rangle \quad (4.3)$$

are assumed to be basis vectors of a two-dimensional *irreducible* corepresentation  $R_j^i$  of the group  $G_j^i + \{K|0\}$   $G_j^i$  since  $|G_j^{ni}\rangle$  and  $|\bar{G}_j^{ni}\rangle$  are eigenstates of  $\tilde{H}$  just as  $|G^n\rangle$  and  $|\bar{G}^n\rangle$  are.

(iii) Operators  $P^n(a)$  which, like the time-inversion operator  $P^n(\{K|0\})$ , do not belong to  $G_j^i$  but commute with  $\tilde{H}$ ,

$$[\tilde{H}, P^n(a)] = 0 \quad \text{for } a \notin G_j^i, \quad (4.4)$$

may have the following effect in order that the state  $|G_j^{ni}\rangle$  is an *eigenstate* of  $\tilde{H}$ : either, also the state  $P^n(a)|G_j^{ni}\rangle$  is the time-inverted state,

$$P^n(a)|G_j^{ni}\rangle = c|\bar{G}_j^{ni}\rangle \quad (4.5)$$

(with  $|c|=1$ ), or the lattice is distorted in such a way that Eq. (4.4) is not satisfied in the incommensurate state.

(iv)  $G_j^i$  must contain symmetry operations associated with the time inversion in order that  $H_j^{ni}$  has real eigenvalues.

(v) The incommensurate state is close to the commensurate as is suggested by the fact that the commensurate structure in Cr can be stabilized by, e.g., alloying with less than 1 at. % Mn.<sup>12</sup>

We now must seek for magnetic groups  $G_j^{ni}$  having corepresentations which satisfy all these conditions. This lengthy examination can be done<sup>9</sup> by means of Table 5.1 of Ref. 10 giving the irreducible representations of all the space groups. Here we only give the results.

##### A. Transversely modulated spin structure

Figure 2 shows a spin-density wave modulated in  $x$  direction. In this paper, this means a transverse modulation since the spins always lie in  $z$  direction. The magnetic group  $G_x^i$  of this structure, i.e., the group  $G_x^i$  having corepresentations which obey all the foregoing conditions, is the group

$$G_x^i = C_{2v}^2 + \{KI|\tau_x\}C_{2v}^2 \quad (4.6)$$

with the orthorhombic primitive Bravais lattice  $\Gamma_o$ . The space group  $C_{2v}^2$  (in the Schönflies notation, see Table 3.7 of Ref. 10) contains, in addition to the translations, the four operations



$$\{E|0\}, \{C_{2x}|\tau_x\}, \{\sigma_z|0\}, \text{ and } \{\sigma_y|\tau_x\} \quad (4.7)$$

[see Eq. (1) of Ref. 11] with the rotation  $C_{2x}$  and the reflection  $\sigma_y$  being associated with the nonprimitive translation  $\tau_x$  as indicated in Fig. 2. It should be noted that  $G_x^i$  does not contain the inversion  $I$  alone but  $I$  is associated with the time inversion  $K$ .

The two corepresentations of the group

$$G_x^i + \{K|0\}G_x^i$$

satisfying all the foregoing conditions are given in the upper part of Table II. The transversely modulated spin-density-wave state  $|G_x^{ni}\rangle$  and the time-inverted state are basis vectors of one of these two corepresentations  $R_x^i$ .

According to the upper part of Table II we get

$$P^n(\{E|\tilde{\mathbf{R}}\})|G_x^{ni}\rangle = e^{-i\hat{\mathbf{Q}}\cdot\tilde{\mathbf{R}}}|G_x^{ni}\rangle \quad (4.8)$$

by application of a translation  $\tilde{\mathbf{R}}$  of the group  $G_x^i$  on  $|G_x^{ni}\rangle$  (with  $G_x^i$  having the basic translations  $\tilde{\mathbf{R}}_x$ ,  $\mathbf{R}_y$ , and  $\mathbf{R}_z$  as given in Figs. 1 and 2). The wave vector  $\hat{\mathbf{Q}}$  of  $|G_x^{ni}\rangle$  cannot be determined completely by group theory but is given by one of the vectors of the points  $U$ ,  $X$ ,  $S$ , or  $R$  in the Brillouin zone of  $\Gamma_o$ ,

$$\hat{\mathbf{Q}} \in \{\mathbf{k}_U, \mathbf{k}_X, \mathbf{k}_S, \mathbf{k}_R\}. \quad (4.9)$$

Equation (4.9) does not state that  $\hat{\mathbf{Q}}$  is not fixed but with our methods we cannot determine  $\hat{\mathbf{Q}}$  more exactly. In order to avoid confusion, we call this vector  $\hat{\mathbf{Q}}$  and the vector  $\mathbf{Q}$  which can be observed by neutron-diffraction experiments,<sup>13</sup> the vector of the spin-density wave and the vector of the modulation of the spin-density wave, respectively. The vector  $\hat{\mathbf{Q}}$  denotes the crystal momentum of the spin-density wave and  $\mathbf{Q}$  is related, in the usual way, to the geometric features of the Fermi surface.

An interesting result is that the two operations associated with the nonprimitive translation  $\tau_x$  cannot be removed from  $G_x^i$  because, otherwise, the corepresentations  $R_x^i$  becomes reducible [which would contradict the assumption (ii) as given earlier]. Therefore, the transversely modulated spin-density wave is not totally incommensurate but the periodicity  $\mathbf{p}_x$  is an even multiple of the lattice constant,

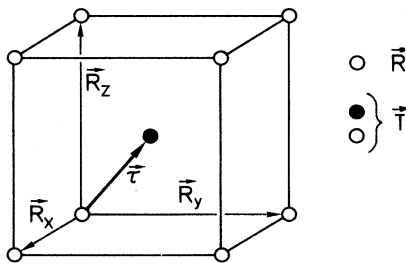


FIG. 1. Black and white Bravais lattice of perfect antiferromagnetic Cr. Everywhere in this paper  $\mathbf{R}$  and  $\mathbf{T}$  denote the translations of the antiferromagnetic and the paramagnetic lattice, respectively.

$$\mathbf{p}_x = 2n\mathbf{R}_x, \quad (4.10)$$

where  $n$  is an integer and  $\mathbf{R}_x$  is the basic translation indicated in Fig. 1. The phases of the magnetic moments separated by

$$\tau_x = n\mathbf{R}_x \quad (4.11)$$

are connected to each other by symmetry. This may be interpreted in terms of long-ranged indirect exchange interactions acting between localized electron states which are separated from each other by about 12 lattice constants (since the experimental values of  $\mathbf{p}_x$  lie between 20 and 27 lattice constants). Equation (4.10) shall be discussed in Sec. V D.

The general condition for  $\mathbf{p}_x$  is

$$\mathbf{p}_x = \frac{m}{m'}\mathbf{R}_x, \quad (4.12)$$

where  $m$  is an even and  $m'$  is an odd integer, since in all these cases  $G_x^i$  contains a nonprimitive translation which is the  $m'$  fold of  $\tau_x$  [as given in Eq. (4.11)]. Thus, if  $m' \geq 3$ , exchange interactions are required acting between atoms which are separated by 36 and more lattice constants. Therefore, in this case, a spin-density wave becomes extremely unstable with respect to small perturbations of the translation symmetry. Perhaps a state with  $m'=3$  may be stable in very pure and perfect crystals. We believe that higher values of  $m'$  are unrealistic.

There are several symmetry operations satisfying Eq. (4.4), namely the inversion, the operation  $\{K|\tau_x\}$ , and all the translations which belong to the commensurate structure but do not belong to  $G_x^i$ . Therefore, according to the above-mentioned third condition, the state  $|G_x^{ni}\rangle$  is accompanied by a slight distortion of the lattice. Figure 3 shows a simple distortion with the group  $D_{2h}^5 = C_{2v}^2 + \{I|\tau_x\}C_{2v}^2$ , i.e., an appropriate distortion. (This group may be written as  $D_{2h}^5 = C_{2v}^2 + \{I|0\}C_{2v}^2$  when the origin of the coordinate system in Fig. 3 lies at point  $I_0$ .) The crystal structure is invariant with respect to the inversion at  $I_0$  (see Fig. 3). This is in accordance with the above-mentioned third condition (iii) because an inversion at  $I_0$  produces the time-inverted spin structure (see Fig. 2).

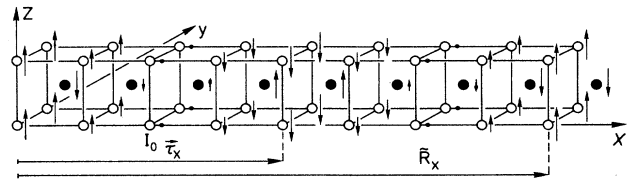


FIG. 2. Transversely modulated spin-density wave with the magnetic group  $G_x^i$  as given in Eq. (4.6).  $\tilde{\mathbf{R}}_x$  is an even multiple of the lattice constant since the nonprimitive translation  $\tau_x$  must belong to  $G_x^i$ . A possible lattice distortion belonging to this spin structure is given in Fig. 3.

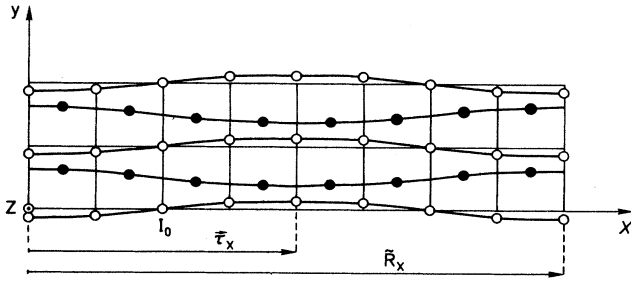


FIG. 3. Possible lattice distortion belonging to the spin structure of Fig. 2.  $I_0$  denotes the center of inversion. By group theory we can neither determine the dimension of the displacements of the atoms nor give the exact form of these distortions. We only know that they have the space group  $C_{2v}^2 + \{I|\tau_x\}C_{2v}^2$  and that the displacements do not vanish since, otherwise, the spin-density-wave state becomes unstable (see Sec. IV).

### B. Longitudinally modulated spin structure

The magnetic group of the longitudinally modulated spin structure can be derived<sup>9</sup> from the preceding five conditions and is given by

$$G_z^i = C_{4h}^1 + \{K\sigma_x|0\}C_{4h}^1 \quad (4.13)$$

with the spin structure being modulated in  $z$  direction. The space group  $C_{4h}^1$  has the tetragonal primitive Bravais lattice,  $\Gamma_q$ , with the Brillouin zone given, e.g., in Fig. 3 of Ref. 11. It contains, in addition to the translations, eight symmetry operations which can be generated from the two operations

$$\{C_{4z}^+|0\} \text{ and } \{I|0\}. \quad (4.14)$$

When the periodicity  $\mathbf{p}_z$  is exactly an odd multiple of the lattice constant, say  $\mathbf{p}_z = 21 \cdot \mathbf{R}_z$ , then the symmetry of the group  $G_z^i$ , as given in Eq. (4.13), is too high. In this case, the inversion  $\{I|0\}$  must be removed and  $G_z^i$  is given by

$$G_z^i = C_4^1 + \{K\sigma_x|0\}C_4^1. \quad (4.15)$$

The two corepresentations  $R_z^i$  of the group  $G_z^i + \{K|0\}G_z^i$  satisfying the above-mentioned five conditions are given in the lower part of Table II.

An important result is that  $G_z^i$  contains no nonprimitive translations. The longitudinally modulated spin-density wave is hence totally incommensurate with the lattice constant because the periodicity  $\mathbf{p}_z$  may accept any value. This result shall be discussed in Sec. V. G.

The wave vector  $\hat{\mathbf{Q}}$  of the spin-density-wave state  $|G_z^{ni}\rangle$  is not fixed by group theory because  $G_z^i$  does not contain nonprimitive translations.  $\hat{\mathbf{Q}}$  is given by one of the vectors of the points  $\Gamma$ ,  $M$ ,  $Z$ , or  $A$  in the Brillouin zone of  $\Gamma_q$ ,

$$\hat{\mathbf{Q}} \in \{0, \mathbf{k}_M, \mathbf{k}_Z, \mathbf{k}_A\} \quad (4.16)$$

since the little groups of these points are identical with the space group  $C_{4h}^1$ . Most likely,  $\hat{\mathbf{Q}} = 0$  may be excluded

since this would violate the fifth condition (v).

Also  $|G_z^{ni}\rangle$  can only be stable if the lattice is slightly distorted. The distortions now are displacements of the atoms in  $z$  direction with the space groups  $D_{4h}^1 = C_{4h}^1 + \{\sigma_x|0\}C_{4h}^1$  and  $C_{4v}^1 = C_4^1 + \{\sigma_x|0\}C_4^1$  in the cases (4.13) and (4.15), respectively.

## V. SUMMARY AND DISCUSSION

### A. Stability of a perfect antiferromagnetic state

Within the nonadiabatic Heisenberg model the “antiferromagnetic” band denoted in Fig. 1 of Ref. 5 by the heavy line is responsible for the stability of the antiferromagnetic state. The condensation energy  $\Delta E$ , i.e., the energy difference between the paramagnetic and the perfect antiferromagnetic state, is given by Eq. (2.9). This “nonadiabatic exchange energy” has the same physical origin as the familiar exchange energy (see Sec. II) and hence is, most likely, responsible for magnetism in further metals.

The condition for itinerant antiferromagnetism reads as follows. In a given metal with the paramagnetic group  $G^P$ , an antiferromagnetic state with the magnetic group  $G^M$  can be stable if the Bloch functions of one of the narrowest, roughly half-filled bands can be unitarily transformed into optimally localizable Wannier functions which are, according to Eqs. (B3)–(B5), symmetry adapted to  $G^M$  and which cannot be chosen symmetry adapted to  $G^P$ . Equations (B3)–(B5) state that, by application of a symmetry operator of  $G^M$ , a Wannier function (which is symmetry adapted to  $G^M$ ) gets transformed into a linear combination of Wannier functions all of them belonging to the *same* atom. The theory of optimally localizable Wannier functions which are symmetry adapted to any given space or magnetic group is given, in detail, in three former papers<sup>14</sup> and, in summary form, in Sec. II of Ref. 5.

The condition for antiferromagnetism is analogous to the condition for superconductivity as given in Ref. 2. It states that, in a given metal with the paramagnetic group  $G^P$ , a superconducting state can be stable if the Bloch functions of one of the narrowest, roughly half-filled bands can be unitarily transformed into optimally localizable spin-dependent Wannier functions which are symmetry adapted to  $G^P$ . Probably, also ferromagnetism produced by local magnetic moments is connected with the existence of Wannier functions being symmetry adapted to the related magnetic groups. Before extending the theory of the present paper to such and other forms of magnetism, the narrowest, roughly half-filled energy bands of other magnetic metals should be searched for the existence of symmetry-adapted Wannier functions.

### B. Theoretical aspects of the new model

Within the nonadiabatic Heisenberg model the magnetic ground state of Cr is still an *eigenstate* of the usual adiabatic electronic Hamiltonian  $\hat{H}$  as given in Eq. (3.28). The new projection operator  $F^n$  [see Eq. (3.26)] selects

from the eigenstates of  $\tilde{H}$  those states which satisfy the Pauli principle within the nonadiabatic system. Thus, the only nonadiabatic phenomenon used in this model is a small shift of the Fermi character at the transition from the adiabatic to the nonadiabatic system: While, within the adiabatic approximation, the Fermi excitations usually are represented by purely electronic states, these excitations are represented, within the nonadiabatic Heisenberg model, by localized states of well-defined symmetry which are occupied by electrons carrying with them some nonadiabatic motion of the nuclei.

The characteristic of the new model is that the symmetry of these nonadiabatic localized states is determined by the symmetry of the Wannier functions belonging to the narrowest, half-filled energy bands of the considered metal. Therefore, predictions as to which exchange effects are possible in this metal can be given. Further, a new exchange effect, namely spin-phonon interaction, becomes apparent. While, in this paper, spin-phonon interaction is only mentioned incidentally in Sec. III B, in Ref. 2 it is proposed to be responsible for superconductivity.

An unmagnetic ground state of any Hamiltonian  $H$  belongs to a one-dimensional representation of the space group  $G$  of  $H$ . This principle appears to be violated for magnetic ordered states since a magnetic structure is transformed, by time inversion, into the opposite structure although the adiabatic Hamiltonian commutes with the time-inversion operator. Within the nonadiabatic Heisenberg model, on the other hand, also a magnetic state belongs to a one-dimensional corepresentation of the group  $G^M$  of the nonadiabatic Hamiltonian  $H^n$  since the projection operator  $F^n$ , and hence also  $H^n$ , does not commute with the time-inversion operator.

The introduction of the projection operator  $F^n$  clearly shows that also linear combinations of the magnetic state and the time-inverted state are eigenstates of the adiabatic Hamiltonian  $\tilde{H}$  (although these states do not satisfy the Pauli principle). This fact suggests (see Sec. III C) that also another group-theoretical theorem is applicable to magnetic states, namely, that the eigenstates of any Hamiltonian  $H$  are basis functions of an *irreducible* (co)representation of the group of  $H$ . On the basis of this assumption, group-theoretical standard procedures can be used for determining the symmetry of magnetic states.

### C. Symmetry of the perfect antiferromagnetic state

The symmetry of the nonadiabatic ground state  $|G^n\rangle$  of Cr is characterized by the fact that, on the one hand,  $|G^n\rangle$  is the ground state of the operator  $H^n$  [as given in Eq. (3.25)] with the magnetic group  $G^M$  and, on the other hand,  $|G^n\rangle$  is an eigenstate of the operator  $\tilde{H}$  [see Eq. (3.28)] which commutes, in contrast to  $H^n$ , with the time-inversion operator. Therefore,  $|G^n\rangle$  belongs to a one-dimensional corepresentation of  $G^M$  and both  $|G^n\rangle$  and the time-inverted state  $|\bar{G}^n\rangle$  belong to a two-dimensional irreducible corepresentation of  $G^M + \{K|0\}G^M$ .

The four possible corepresentations  $R^T$  [which only differ by unessential factors  $d(\alpha)=\pm 1$ ] to which  $|G^n\rangle$

and the time-inverted state  $|\bar{G}^n\rangle$  can belong are given in Table I. A remarkable result is that  $|G^n\rangle$  is an  $N$ -electron Bloch state with wave vector  $\hat{Q}=\mathbf{k}_M$  [cf. Eq. (3.37)] where  $\mathbf{k}_M$  is the vector of the point  $M$  in the Brillouin zone of perfect antiferromagnetic Cr (as depicted, e.g., in Fig. 3 of Ref. 11). Therefore,  $|G^n\rangle$  can be interpreted in terms of a static spin-density wave being a superposition of two helical waves with wave vectors  $\mathbf{k}_M$  and  $-\mathbf{k}_M$ , respectively, since both vectors are equivalent within the antiferromagnetic Brillouin zone. The vector  $\hat{Q}$  cannot be directly observed by neutron-diffraction experiments since  $M$  is not a point of the reciprocal antiferromagnetic lattice.

### D. Symmetry of the transversely modulated spin-density wave

The symmetry properties of the transverse spin-density wave have been determined by starting from the five conditions given at the beginning of Sec. IV and are summarized in Sec. IV A.

One result is that the transverse spin-density-wave state  $|G_x^{ni}\rangle$  is not quite incommensurate but its periodicity  $\mathbf{p}_x$  is an even multiple of the lattice constant. (In very perfect and pure crystals we cannot exclude that  $\mathbf{p}_x$  may also be an even multiple of a third of the lattice constant.) This result appears to contradict the accurate experiments on the temperature dependence of the periodicity showing that  $\mathbf{p}_x$  varies continuously with temperature from about 21 to 28 lattice constants.<sup>15</sup> An interpretation of these experiments which is consistent with our result is that the observed magnetic structure is a polydomain rather than a single- $\mathbf{p}_x$  state. On cooling of the sample, for instance, the periodicity of the spin system does not flip as a whole from, say, 24 to 22 lattice constants but small domains with a periodicity of 22 lattice constants arise which continuously grow on cooling.

The atoms which are separated by  $\tau_x$ , that is, by about 12 lattice constants, are coupled to each other by long-ranged indirect antiferromagnetic exchange interaction so that this state is very unstable with respect to small perturbations of the translation symmetry. This may be the reason why the magnetic structure becomes abruptly commensurate by alloying with about 1 at. % other transition metals.<sup>12</sup>

The wave vector  $\hat{Q}$  of  $|G_x^{ni}\rangle$  (i.e., the crystal momentum of  $|G_x^{ni}\rangle$ ) cannot be determined uniquely by group theory; its possible values are given by Eq. (4.9). According to the fifth condition (v) given in Sec. IV it might be that

$$\hat{Q}=\mathbf{k}_S, \quad (5.1)$$

because, in this case,  $\hat{Q}$  is close to the wave vector of the perfect antiferromagnetic state [cf. Eq. (3.38)]. This question, however, cannot yet be answered finally.

### E. Symmetry of the longitudinally modulated spin-density wave

The symmetry properties of the longitudinal spin-density-wave state  $|G_z^{ni}\rangle$  are summarized in Sec. IV B. In

contrast to  $|G_x^{ni}\rangle$ , the state  $|G_z^{ni}\rangle$  is totally incommensurate with the lattice constant. In Sec. V G we speculate that this behavior might be responsible for the spin-flip transition.

In the group  $C_{4h}^1$  the localized states with spin-down and spin-up direction are not connected by symmetry as this is the case in the group  $C_{2v}^2$ . Therefore, the magnetic moments of these states may be accidentally equal or, more probably, slightly different. Thus, we cannot exclude that the longitudinally modulated spin structure is slightly ferrimagnetic whereas the transversely modulated structure is exactly antiferromagnetic.

The wave vector  $\hat{Q}$  of  $|G_z^{ni}\rangle$  cannot be determined uniquely, too; its possible values are given by Eq. (4.16). We believe that

$$\hat{Q} = \mathbf{k}_A, \quad (5.2)$$

because, in this case,  $\hat{Q}$  is close to, but slightly different from, the wave vector of the perfect antiferromagnetic state.

#### F. Stability of the incommensurate spin-density-wave states

To a first approximation, the band structure of antiferromagnetic Cr is obtained by folding the energy bands of paramagnetic Cr into the antiferromagnetic Brillouin zone as given, e.g., in Fig. 4, Fig. 63, and Fig. 2 of Ref. 16, Ref. 17, and Ref. 11, respectively. A peculiar feature of this band structure is the band intersections along the lines  $\Gamma M$  and  $\Gamma A$  (in the notation given in Fig. 2 of Ref. 11) slightly above the Fermi energy. If an energy gap is formed at these points, the depression of the occupied states below these gaps leads to a lowering of the total electronic energy (see, e.g., the detailed consideration in Sec. IV of Ref. 17).

As shown in Ref. 11, these band degeneracies are not removed in the perfect antiferromagnetic state. From Table II of Ref. 11, however, it follows immediately that they split if the operations  $\{\sigma_{db}|\tau\}$  and  $\{C_{2a}|\tau\}$  are taken out of the space group. Thus, they split in the incommensurate states since neither  $C_{2v}^2$  nor  $C_{4h}^1$  contains these operations. This result suggests that the perfect antiferromagnetic state is unstable with respect to the formation of an incommensurate spin-density-wave state. The stabilization energy of this state, i.e., the energy difference between the *perfect* and the incommensurate antiferromagnetic state, we therefore assume to originate from a splitting of the degeneracies at the commensurate-incommensurate transition.

This assumption is corroborated by self-consistent band-structure calculations<sup>16,18</sup> of antiferromagnetic Cr, all of them showing energy gaps at the said positions which are generally thought to stabilize the antiferromagnetic state. It should be noted that these calculations use the group  $O_h^1$ , the group of CsCl, as the space group of antiferromagnetic Cr. Therefore, these calculations are related to the incommensurate state rather than to the commensurate spin structure since the group  $O_h^1$  produces the same band splittings near the Fermi level as the space groups  $C_{2v}^2$  and  $C_{4h}^1$  of the incommensurate spin

arrangements (while, according to Fig. 2 of Ref. 11, the group  $O_h^1$  and the space group  $D_{4h}^6$  of the perfect antiferromagnetic state produce different band splittings). The energy gain arising from the formation of energy gaps at the Fermi energy hence occurs at the commensurate-incommensurate transition rather than at the transition from the paramagnetic to the antiferromagnetic state.

#### G. Spin-flip transition

The symmetry properties of the two incommensurate spin-density-wave states may lead to a theoretical understanding of the spin-flip transition which is observed at  $T_{sf} = 123$  K. According to the accurate measurements of Werner and Arrott<sup>15</sup> the parameter of periodicity  $p$  has the value  $p = 21,1$  at the spin-flip transition (corresponding to a periodicity of 21,1 lattice constants). Thus, the transversely modulated spin-density wave forms, slightly above  $T_{sf}$ , a multi- $p$ -domain spin state consisting of domains with  $p = 20$  and 22. On cooling through the spin-flip transition, the spin-density-wave state becomes a single- $p$  state with  $p$  varying continuously from 21,1 to 20,7 at zero temperature since the periodicity  $p$  of the longitudinally modulated spin-density-wave state need not be even.

Assume a single- $p$ -transverse spin-density-wave state to have a (slightly) lower energy than a single- $p$ -longitudinal state, say, because the former state has a higher translation symmetry than the latter. Then the cause for the spin-flip transition might be that, at zero temperature, a *single- $p$*  state, as the state with the highest order, has the lowest energy. In this case, the electron system would undergo the spin-flip transition because the periodicity, which is determined by the nesting vector of the Fermi surface, is not accidentally an even multiple of the lattice constant at zero temperature.

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#### APPENDIX A: SYMMETRY GROUP OF CHROMIUM

In the magnetic group

$$G^M = D_{4h}^6 + \{K|\tau\}D_{4h}^6 \quad (A1)$$

of commensurate antiferromagnetic chromium the time-inversion operator  $K$  is associated with the nonprimitive translation  $\tau = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  denoted in Fig. 1. The space group  $D_{4h}^6$  has the tetragonal point group  $D_{4h}$  containing the sixteen elements listed, e.g., in Eq. (1) of Ref. 11. Eight elements of  $D_{4h}$ , namely the elements of the group  $C_{4h}$  [see Eq. (3) of Ref. 11] are, on their own, symmetry operations of  $D_{4h}^6$  while the remaining elements of  $D_{4h}$  are associated with the nonprimitive translation  $\tau$ .

$G^M$  is a subgroup of the paramagnetic group

$$G^P = O_h^9 + \{K|0\}O_h^9 \quad (A2)$$

of Cr with the body-centered-cubic space group  $O_h^9$ . In this paper we also consider the paramagnetic body-

centered tetragonal group

$$G^T = D_{4h}^{17} + \{K|0\}D_{4h}^{17} \quad (\text{A3})$$

which is also a subgroup of  $G^P$ . The space group  $D_{4h}^{17}$  (in the usual Schönflies notation) has the same point group, namely  $D_{4h}$ , as the antiferromagnetic space group  $D_{4h}^6$  but no nonprimitive translations. It also has the Bravais lattice given in Fig. 1, but with black and white not being distinguished. Thus,  $G^T$  may be written as

$$G^T = G^M + \{E|\tau\}G^M \quad (\text{A4})$$

or

$$G^T = G^M + \{K|0\}G^M \quad (\text{A5})$$

with  $E$  denoting the identity operation.

The space-group operations we denote by

$$a = \{\alpha|t\} \quad (\text{A6})$$

where  $\alpha$  stands for a point group operation and  $t$  is the translation

$$t = \mathbf{R} + \tau(\alpha) \quad \text{for } a \in D_{4h}^6 \quad (\text{A7})$$

and

$$t = \mathbf{T} \quad \text{for } a \in O_h^9. \quad (\text{A8})$$

Everywhere in this paper  $\mathbf{R}$  and  $\mathbf{T}$  denote the primitive translations of the antiferromagnetic and the paramagnetic lattice, respectively. That means,  $\mathbf{R}$  is related to the, say, white lattice points in Fig. 1 and  $\mathbf{T}$  is related to both the black and white lattice points. The nonprimitive translation  $\tau(\alpha)$  is defined by

$$\tau(\alpha) = \begin{cases} 0 & \text{for } \alpha \in C_{4h} \\ \tau & \text{for } \alpha \in D_{4h} - C_{4h}. \end{cases} \quad (\text{A9})$$

The symmetry operators  $P(a)$  act on a function of position,  $f(\mathbf{r})$ , according to

$$P(\{\alpha|t\})f(\mathbf{r}) = f(\alpha^{-1}\mathbf{r} - \alpha^{-1}t) \quad (\text{A10})$$

and

$$P(\{K|\tau\})f(\mathbf{r}) = f^*(\mathbf{r} - \tau). \quad (\text{A11})$$

## APPENDIX B: SYMMETRY-ADAPTED WANNIER FUNCTIONS IN CHROMIUM

The Bloch functions of the AF band of Cr (see Fig. 1 of Ref. 5) can be unitarily transformed into optimally localized Wannier functions

$$w_1(\mathbf{r} - \mathbf{R}).$$

and

$$w_2(\mathbf{r} - \mathbf{R} - \tau) = w_1^*(\mathbf{r} - \mathbf{R} - \tau), \quad (\text{B1})$$

as given in Eqs. (2.42) and (2.43) of Ref. 5, which are, according to Eqs. (2.44) and (2.45) of Ref. 5, symmetry adapted to the antiferromagnetic group  $G^M$ .

Writing the Wannier functions as

$$\langle \mathbf{r}|\mathbf{T} \rangle = \begin{cases} w_1(\mathbf{r} - \mathbf{R}) & \text{for } \mathbf{T} = \mathbf{R} \\ w_2(\mathbf{r} - \mathbf{R} - \tau) & \text{for } \mathbf{T} = \mathbf{R} + \tau, \end{cases} \quad (\text{B2})$$

we can write Eqs. (2.44) and (2.45) of Ref. 5 in the form<sup>9</sup>

$$P(\{\alpha|\tau(\alpha)\})\langle \mathbf{r}|\mathbf{T} \rangle = d(\alpha)\langle \mathbf{r}|\alpha\mathbf{T} + \tau(\alpha) \rangle \quad \text{for } \alpha \in D_{4h} \quad (\text{B3})$$

[with  $d(\alpha) = \pm 1$ , see Eq. (2.48) of Ref. 5] and

$$P(\{K|\tau\})\langle \mathbf{r}|\mathbf{T} \rangle = \langle \mathbf{r}|\mathbf{T} + \tau \rangle. \quad (\text{B4})$$

Additionally, Eq. (B2) gives

$$P(\{E|\mathbf{R}\})\langle \mathbf{r}|\mathbf{T} \rangle = \langle \mathbf{r}|\mathbf{T} + \mathbf{R} \rangle \quad (\text{B5})$$

with  $E$  denoting the identity operation.

The effect of the time-inversion operator  $P(\{K|0\})$  cannot be given by a simple equation like Eq. (B4) because  $\{K|0\}$  does not belong to  $G^M$  and it is not possible<sup>9</sup> to assign to the AF band Wannier functions which are symmetry adapted to the group  $G^T$  [see Eq. (A5)]. Therefore,<sup>9</sup>  $P(\{K|0\})\langle \mathbf{r}|\mathbf{T} \rangle$  is a linear combination of Wannier functions belonging to the AF band,

$$P(\{K|0\})\langle \mathbf{r}|\mathbf{T} \rangle = \sum_{\mathbf{T}'} d(\mathbf{T}, \mathbf{T}')\langle \mathbf{r}|\mathbf{T}' \rangle, \quad (\text{B6})$$

with

$$\sum_{\mathbf{T}'} |d(\mathbf{T}, \mathbf{T}')|^2 = 1 \quad (\text{B7})$$

and at least two nonvanishing coefficients, say,

$$d(\mathbf{T}, \mathbf{T}'_1) \neq 0 \quad \text{and} \quad d(\mathbf{T}, \mathbf{T}'_2) \neq 0, \quad (\text{B8})$$

where  $\mathbf{T}'_1 \neq \mathbf{T}'_2$ .

Each localized state  $|\mathbf{T}\rangle$  may be occupied by an electron with spin-down or spin-up direction. We put

$$\langle \mathbf{r}, t|\mathbf{T}, s \rangle = \langle \mathbf{r}|\mathbf{T} \rangle u_s(t), \quad (\text{B9})$$

where  $s = \pm \frac{1}{2}$  denotes the two spin directions,  $t = \pm \frac{1}{2}$  is the spin coordinate, and

$$u_s(t) = \delta_{s,t}$$

are Pauli's spin functions. An operator  $S(\alpha)$  of the three-dimensional rotation group,  $O(3)$ , acts on  $u_s(t)$  according to

$$S(\alpha)u_s(t) \equiv u_s(\alpha^{-1}t), \quad (\text{B10})$$

where

$$u_s(\alpha^{-1}t) = \sum_{s'} D_{s's}(\alpha)u_{s'}(t) \quad \text{for } \alpha \in O(3) \quad (\text{B11})$$

with the matrices  $D_{s's}(\alpha)$  belonging to the two-dimensional double-valued representation  $D_{1/2}$  of  $O(3)$ . The effect of the time-inversion operator we write as

$$S(K)u_s(t) \equiv u_s(Kt), \quad (\text{B12})$$

where

$$u_s(Kt) = g_s(K)u_{-s}(t) \quad (\text{B13})$$

with

$$g_{\pm 1/2}(K) = \mp i . \quad (\text{B14})$$

For the operators of the tetragonal point group,  $D_{4h}$ , Eq. (B11) simply reads

$$S(\alpha)u_s(t) = g_s(\alpha)u_{\alpha s}(t) \text{ for } \alpha \in D_{4h} , \quad (\text{B15})$$

where the  $c$  numbers  $g_s(\alpha)$ , with

$$|g_s(\alpha)| = 1 ,$$

are given, e.g., in Table 6.7 of Ref. 10 and

$$\alpha s = \begin{cases} s & \text{for } \alpha \in C_{4h} \\ -s & \text{for } \alpha \in D_{4h} - C_{4h} . \end{cases} \quad (\text{B16})$$

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