

## Energy Bands in Paramagnetic Chromium\*

J. Rath and J. Callaway

*Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803*

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The results of a self-consistent tight-binding calculation of the band structure of paramagnetic chromium are reported. The basis set consisted of atomic wave functions for the  $1s$ ,  $2s$ ,  $3s$ ,  $4s$ ,  $2p$ ,  $3p$ , and  $4p$  states expressed as linear combinations of Gaussian-type orbitals (GTO) and five individual GTO's for each  $3d$  state. The exchange potential was calculated according to the  $X\alpha$  method with  $\alpha=2/3$ . The initial Coulomb potential was constructed from the superposed charge densities of neutral chromium atoms in a  $3d^5 4s^1$  configuration. Eleven iterations were required to determine a self-consistent potential. The charge density was sampled at 55 inequivalent points in  $1/48$  of the Brillouin zone. Energy bands were calculated with the use of the self-consistent potential at 819 points in  $1/48$  of the zone. The density of states was calculated according to the Gilat-Raubenheimer method. Cross sections of the Fermi surface were obtained in several symmetry planes. The x-ray form factor was determined from the self-consistent wave functions.

### I. INTRODUCTION

The band structure of chromium is of considerable interest in view of its antiferromagnetic properties. The antiferromagnetic structure which exists below the Neél temperature of  $312^\circ\text{K}$  has a periodicity incommensurate with that of the lattice and is interpreted in terms of spin-density waves first described by Overhauser.<sup>1,2</sup>

Overhauser showed that the ground state of a free-electron gas in the Hartree-Fock approximation is not paramagnetic, but is, instead, an antiferromagnetic spin-density-wave state. Subsequently, Hamann and Overhauser,<sup>3</sup> Rajagopal,<sup>4</sup> and Fedders and Martin<sup>5</sup> demonstrated that when the screening of electron interactions is included, a ground state of the normal type is obtained. The situation is more complicated when a periodic potential is present. Special features of the Fermi surface in the paramagnetic state can produce an instability leading to the formation of an antiferromagnetic ground state.

What is required is "nesting." If it is possible to translate portions of electron sheets of the Fermi surface by some wave vector  $\vec{Q}$  so that they come into coincidence with similarly shaped hole sheets, the magnetic susceptibility of the paramagnetic state may develop a maximum near  $\vec{Q}$ . Such a situation favors the formation of spin-density waves of this  $\vec{Q}$ . Lomer pointed out that these conditions should be realized in chromium.<sup>6</sup> These arguments require modification because nesting is not perfect, and because matrix elements may vary strongly in the vicinity of the surfaces on which nesting occurs.<sup>7</sup>

It then becomes of interest to study the band structure and electronic wave functions of chromium in detail. Several calculations have been reported previously.

Asdente and Friedel<sup>8</sup> and Asdente<sup>9</sup> calculated the  $d$ -band structure and Fermi surface of chro-

mium using a crude form of tight-binding method. These authors made drastic approximations concerning the crystal potential, the wave functions, and the tight-binding matrix elements and were unable to obtain results of quantitative significance. The essential features of the Fermi surface including those responsible for the nesting were inferred by Lomer<sup>6,10</sup> from the results of a calculation performed for iron by Wood.<sup>11</sup> The portions of particular interest are closed electron and hole surfaces around  $\Gamma$  and  $H$ , respectively, hole pockets around  $N$ , and electron balls along the  $[100]$  axis. Similar conclusions were inferred by Mattheiss from a band calculation for tungsten.<sup>12</sup>

These surfaces have also been obtained in specific band calculations for chromium. The first of these was an augmented-plane-wave (APW) computation by Loucks.<sup>13</sup> This work employed a potential obtained from a superposition of atomic charge densities. Exchange was included in the  $\rho^{1/3}$  approximation ( $X\alpha$  with  $\alpha=1$ ). The calculation was not carried to self-consistency. The Fermi surface obtained by Loucks was in qualitative agreement with Lomer's model except that no hole pockets were obtained at  $N$ . No value for the nesting wave vector  $\vec{Q}$  was reported. Switendick reported briefly results for charge and spin densities obtained from a self-consistent form of the APW method, but experienced difficulties in obtaining convergence to the proper antiferromagnetic state as the number of iterations was increased.<sup>14</sup>

Asano and Yamashita applied the Korringa-Kohn-Rostoker (KKR) (Green's-function) method in a calculation of band structures in both paramagnetic and antiferromagnetic phases of chromium.<sup>15</sup> They carried their calculation to approximate self-consistency. Exchange was included as in the work of Loucks ( $X\alpha$ ,  $\alpha=1$ ), and a somewhat *ad hoc* correlation correction was imposed in the spirit of the Wigner-Seitz method. In the case of antiferro-

TABLE I. Fourier coefficients of the Coulomb and exchange potentials for paramagnetic chromium are listed for the smallest 20 reciprocal-lattice vectors. The quantities  $\Delta V$  are the changes in these quantities from the first to the final iteration.

$\vec{K}$	$V_c(\vec{k})$	$\Delta V_c(\vec{k})$	$V_{ex}(\vec{k})$	$\Delta V_{ex}(\vec{k})$
[000]	-1.7060	0.2452	-1.3072	-0.0905
[110]	-0.8136	-0.0933	-0.2200	0.0228
[200]	-0.5979	-0.0293	-0.0251	0.0163
[211]	-0.4785	-0.0067	-0.0377	-0.0031
[220]	-0.3992	-0.0019	-0.0522	-0.0104
[310]	-0.3420	0.0022	-0.0395	-0.0075
[222]	-0.2987	0.0008	-0.0161	-0.0015
[321]	-0.2649	0.0004	0.0012	0.0029
[400]	-0.2377	-0.0011	0.0067	0.0043
[411]	-0.2155	-0.0003	0.0024	0.0033
[330]	-0.2155	0.0004	0.0024	0.0033
[420]	-0.1971	0.0000	-0.0063	-0.0011
[332]	-0.1816	0.0006	-0.0142	-0.0010
[422]	-0.1683	0.0003	-0.0184	-0.0023
[510]	-0.1569	-0.0003	-0.0183	-0.0026
[431]	-0.1569	0.0003	-0.0183	-0.0026
[521]	-0.1383	-0.0000	-0.0098	-0.0010
[440]	-0.1307	0.0002	-0.0048	0.0000
[433]	-0.1239	0.0003	-0.0011	0.0009
[530]	-0.1239	0.0001	-0.0011	0.0009

magnetic chromium, they considered a hypothetical state in which the wave vector  $Q$  is exactly half a reciprocal-lattice vector ( $2\pi/a$ ). They obtained a Fermi surface for paramagnetic chromium consistent with Lomer's model. Although their procedure differs in many respects from ours, the resulting Fermi surface is rather similar to ours. A detailed comparison of the present results with those of Asano and Yamashita will be given subsequently (Table II).

Additional band calculations for paramagnetic

chromium have been reported by Yasui, Hayashi, and Shimizu,<sup>1</sup> and by Gupta and Sinha.<sup>7</sup> Yasui *et al.* employed a combination of tight-binding and orthogonalized-plane-wave (OPW) methods, the tight-binding portion being done in the manner of Stern<sup>17</sup> in which wave functions are added so that all integrals may be performed in a single cell. The calculations were carried to self-consistency for two values of the exchange parameter  $\alpha$  in the  $X\alpha$  method ( $\alpha = 1.0$  and  $0.725$ ). The Fermi surface obtained for  $\alpha = 1$  was not in good agreement with that required to produce the observed antiferromagnetic structure, whereas good results were obtained for  $\alpha = 0.725$ . This is consistent with our experience in that we find that transition-metal band structures computed self-consistently with  $\alpha = 1$  are unsatisfactory,<sup>18</sup> and that a value of  $\alpha$  close to the Kohn-Sham-Gaspar<sup>19</sup> result ( $\frac{2}{3}$ ) gives better results. A comparison of some features of the results of Yasui *et al.* with those obtained here is also presented in Table II.

In the course of a calculation of the wave-vector-dependent magnetic susceptibility of chromium, Gupta and Sinha<sup>7</sup> reported a computation of the band structure according to the APW method ( $X\alpha$  with  $\alpha = 1$ ). This calculation was not iterated to self-consistency, and some aspects of the band structure are inconsistent with ours as well as those of Asano and Yamashita and Yasui *et al.* They obtained a value of 0.88 for the nesting wave vector (in units of  $2\pi/a$ ). A detailed comparison of their results with ours is also included in Table II.

## II. METHOD

The present calculation is an application of the tight-binding or linear-combination-of-atomic-or-

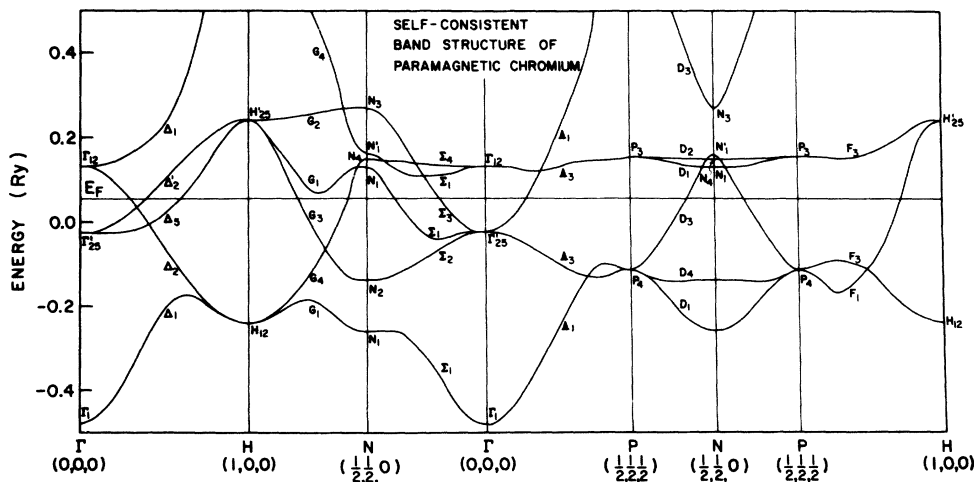


FIG. 1. Energy bands in paramagnetic chromium along certain symmetry directions.

TABLE II. Energy differences between certain states at symmetry points (in Ry) according to four calculations.

	Asano and Yamashita (Ref. 15)	Gupta and Sinha (Ref. 7)	Yasui <i>et al.</i> (Ref. 16)	Present
$\Gamma_{12}-\Gamma_1$	0.5785	0.709	0.569	0.6102
$\Gamma_{12}-\Gamma'_{25}$	0.1332	0.136	0.145	0.1590
$\Gamma'_{25}-\Gamma_1$	0.4452	0.573	0.424	0.4513
$H'_{25}-H_{12}$	0.4848	0.523	0.467	0.4812
$H_{15}-\Gamma_1$	...	1.330	1.097	1.2644
$H'_{25}-\Gamma'_{25}$	0.2341	0.238	0.298	0.2670
$\Gamma_{12}-H_{12}$	0.3840	0.421	0.314	0.3730
$P_3-P_4$	0.2505	0.300	0.227	0.2670
$N_2-N_1$	0.1326	0.170	0.109	0.1234
$N_3-N_1$	0.5025	0.558	0.498	0.5302
$N_4-N_1$	0.0200	...	...	0.0211
$N'_1-N_4$	0.0530	...	...	0.0115
$N_3-N'_1$	0.0498	...	0.069	0.1087

bitals (LCAO) method previously used to study the band structures of nickel<sup>18,20</sup> and iron.<sup>21</sup> The wave function for a Bloch state of wave vector  $\vec{k}$  in band  $n$  is expanded in a set of basis functions  $\phi_i(\vec{k}, \vec{r})$  which are constructed from a set of localized functions,  $u_i(\vec{r} - \vec{R}_\mu)$

$$\psi_n(\vec{k}, \vec{r}) = \sum_i c_{ni}(\vec{k}) \phi_i(\vec{k}, \vec{r}) = \frac{1}{N^{1/2}} \sum_{i\mu} c_{ni}(\vec{k}) e^{i\vec{k} \cdot \vec{R}_\mu} u_i(\vec{r} - \vec{R}_\mu). \quad (1)$$

In the present case, 38 functions  $u_i$  are considered. These functions are either individual Gaussian-type orbitals (GTO) or linear combinations of GTO. Atomic wave functions determined by Wachters<sup>22</sup> were used for states other than  $3d$  ( $1s$ ,  $2s$ ,  $3s$ ,  $4s$ ,  $2p$ ,  $3p$ ,  $4p$ ). In order to describe the  $d$ -band wave functions, five radial GTO were introduced for each of the five possible  $l=2$  angular functions. The exponents used in defining these functions were those employed by Wachters in his calculation for atomic chromium.

The calculation was begun by constructing a crystal potential from a superposition of overlapping neutral-atom charge densities, the atoms being assumed to be in the configuration  $3d^5 4s^1$ . Exchange was included according to the  $X\alpha$  method.<sup>23</sup> Our previous work on transition-metal band structures indicates that values of  $\alpha$  close to  $\frac{2}{3}$  appear to give satisfactory results, and  $\alpha$  was taken as equal to  $\frac{2}{3}$  here. No spin polarization of the chromium atoms was assumed and spin-orbit coupling was also neglected.

Self-consistency was obtained by an iterative procedure in which the wave functions obtained at one stage of the calculation are used to generate Fourier coefficients of the Coulomb potential for the next stage.<sup>24</sup> The calculation of the corrected exchange potential is more cumbersome, as the charge density in a unit cell must be reconstructed.<sup>23</sup> The criterion used to define self-consistency was that the Fourier coefficients of the Coulomb potential should be stable to 0.001 Ry. It was found that only the Fourier coefficients of the smallest 20 rotationally independent reciprocal-lattice vectors were appreciably affected by the self-consistent procedure. Eleven iterations were necessary to achieve self-consistency. The first four iterations were based on wave functions obtained at 14 inequivalent points in  $\frac{1}{48}$ th of the Brillouin zone; the final seven iterations employed 55 points. The exchange potential was found to converge more rapidly than the Coulomb potential. The Fourier coefficients for the smallest 20  $\vec{K}$ 's are given in Table I.

The self-consistent potential was subsequently employed to calculate energy levels at 819 inequivalent points in  $\frac{1}{48}$ th of the Brillouin zone. The density of states was then calculated according to the Gilat-Raubenheimer method.<sup>25</sup>

### III. RESULTS

#### A. Band Structure and Density of States

The calculated band structure is shown along certain symmetry directions in Fig. 1. Some energy differences between states at symmetry points are listed in Table II, where they are compared with results obtained by Asano and Yamashita,<sup>15</sup> Yasui *et al.*,<sup>16</sup> and Gupta and Sinha.<sup>7</sup> The calculations are only roughly comparable because of the

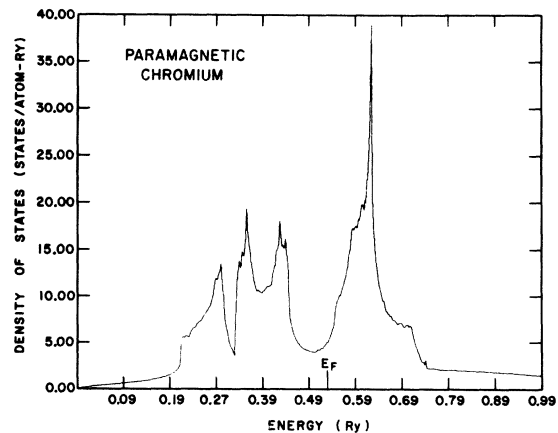


FIG. 2. Density of states of paramagnetic chromium for a single direction of spin.

TABLE III. Description of the Fermi surface.

I	Large electron surface about $\Gamma$	Approximately octahedral.
II	Large hole surface about $H$	Approximately octahedral and slightly larger than surface I. Touches surface IV at six points along $\Gamma$ - $H$ directions at distance $0.41(2\pi/a)$ from $H$ points.
III	Small hole surface about $N$	Ellipsoidal with nearly circular cross section in the $\Gamma NR$ plane, and elliptical cross section in $\Gamma HN$ plane. No intersections with any surfaces.
IV	Electron ball	Almost spherical with greatest deviation from a sphere in $\Gamma$ - $H$ direction. Touches surface II, and intersects surface I. This surface and surface I form the electron "jack."

differences in the value of the exchange parameter. However, the two calculations listed in the table which use  $\alpha = 1$  do not agree well with each other, particularly in the relation of the  $s$  and  $d$  bands. Moreover, there does not seem to be any obvious regular dependence of the energy differences on the value of  $\alpha$ , as would be expected. We know no specific explanation for the irregular behavior.

The calculated density of states is shown in Fig. 2. The density of states at the Fermi energy was found to be  $9.6 \text{ Ry}^{-1}$ . This leads to a value of the coefficient of the linear term in the electronic specific heat of  $1.6 \times 10^{-3} \text{ J/mole } ^\circ\text{K}$ . Since this value pertains to a paramagnetic state, it cannot be compared directly with the results of low-temperature measurements, which are made on antiferromagnetic chromium. However, an experimental value for this coefficient can be estimated by extrapolation from measurements of the specific heats of Cr-Mo and Cr-W alloys to be  $\gamma = 2.9 \times 10^{-3} \text{ J/mole } ^\circ\text{K}$ .<sup>26</sup> Part of the discrepancy may be attributed to neglect of the electron-phonon interaction.

#### B. Optical Absorptions

Studies of the optical properties of chromium may furnish some experimental evidence concerning the band structure. Bos and Lynch<sup>27</sup> have investigated the optical absorption in the energy range in which interband transitions would be expected to be important. They find a broad absorption peak between 1 and 2 eV, with indications of a shoulder near 2 eV, and an additional peak near

3.4 eV. Lenham and Treherne find sharper structure, with peaks at 1.3 and 2.0 eV.<sup>28</sup> Since we have not made a detailed calculation of optical matrix elements, we cannot specify the location of maxima in a precise way. It seems probable to us, on the basis of an examination of the band structure as shown in Fig. 1, that large regions of  $k$  space are involved in all the transitions. Specifically, we would expect a broad region of strong absorption from 1.3 to 2.1 eV with a maximum near 2.0 eV associated with a  $\Sigma_1$ - $\Sigma_3$  transition. These bands are roughly parallel with a separation close to 2.0 eV over a range of  $k$ . Higher-energy absorption associated with  $\Delta_5$ - $\Delta_1$ ,  $P_4$ - $P_3$ , and  $F_3$ - $F_3$  transitions is likely. The latter transitions correspond to energies close to the peak reported at 3.4 eV.

#### C. Fermi Surface

We have made a detailed study of the Fermi surface of paramagnetic chromium. The Fermi surface consists of electron and hole octahedra around  $\Gamma$  and  $H$ , respectively, an electron ball on the  $[100]$  axis, and an ellipsoidal hole pocket around  $N$ . These results are qualitatively in accord with the Lomer model and the results of other calculations. A detailed description of the Fermi surface is given in Table III. Some cross sections are shown in Figs. 3 and 4.

The electron and hole octahedra exhibit the nesting property required by current theories of the antiferromagnetism of chromium. The quantity  $1-\delta$  defined in Fig. 3 describes the nesting. This quantity ranges from 0.976 to 0.955 in the  $(100)$

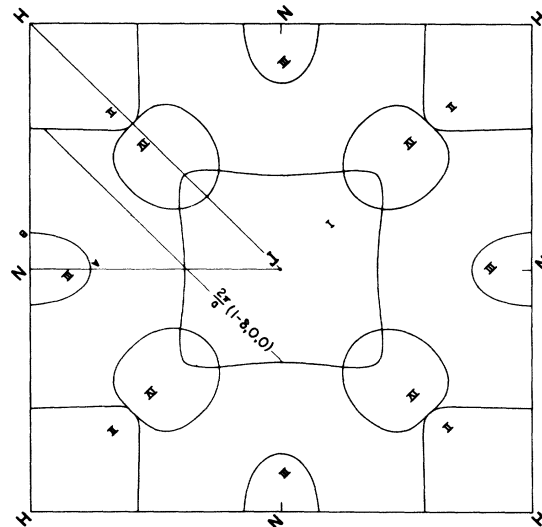


FIG. 3. Cross section of the Fermi surface in the  $(100)$  plane.

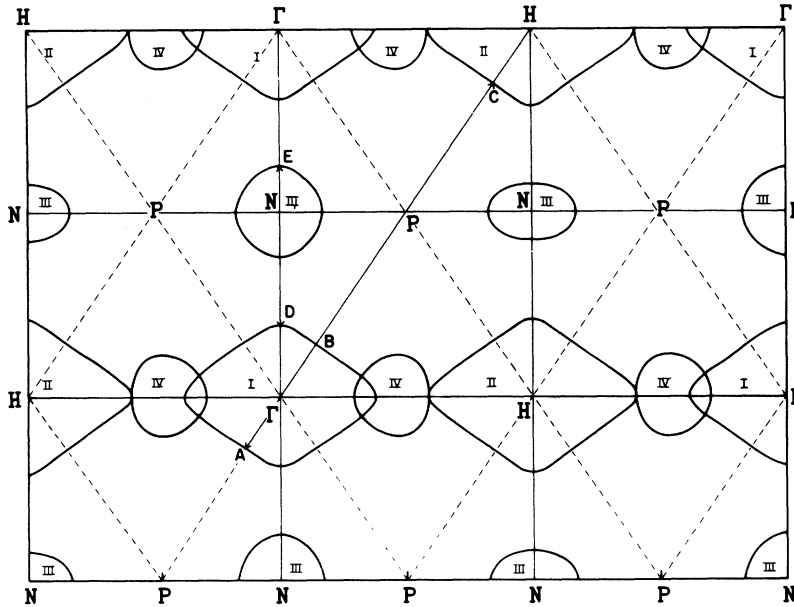


FIG. 4. Composite of cross sections of the Fermi surface in different planes.

plane and from 0.974 to 0.963 in a plane displaced by the vector  $(2\pi/a)(0, 0, \frac{1}{2})$ . The experimental value for  $Q$  is 0.963 close to the Néel temperature and 0.951 at low temperatures.<sup>29</sup> The higher theoretical value which is obtained on the [100] axis probably does not specify the most likely value of  $\tilde{Q}$  since the contribution of states at this point to the magnetic susceptibility is suppressed by symmetry considerations concerning the matrix elements. A detailed numerical calculation of the magnetic susceptibility is required to specify a precise predicted value for the wave vector of the spin-density wave.

Some direct information concerning the Fermi surface of paramagnetic chromium can be obtained from the measurements by Muhlestein and collaborators<sup>30, 31</sup> of the phonon dispersion relations using a neutron-diffraction technique. These authors observed Kohn anomalies<sup>32</sup> in the vibration spectrum both below and above the Néel temperature. Values are reported for the lengths of the vectors AC and ED in Fig. 4. Our results, in units of  $2\pi/a$ , are (with the experimental values in parentheses):

$\vec{k}$	Expt. (Ref. 34)	Theory
[110]	$15.74 \pm 0.2$	16.27
[200]	$13.06 \pm 0.17$	13.31
[211]	$11.37 \pm 0.15$	11.60
[220]	$10.10 \pm 0.14$	10.33
[330]	...	7.510
[411]	...	7.448
[330]/[411]	$1.013 \pm 0.007$	1.008

AC, 0.98 (0.98); ED, 0.427 (0.425).

Experimental information also exists concerning the dimensions of the hole pocket at  $N$ . This comes from measurements of the de Haas-van Alphen effect in the antiferromagnetic state reported by Graebner and Marcus.<sup>33</sup> These authors find that the pocket is ellipsoidal with dimensions of 0.173, 0.234, and 0.268  $\text{\AA}^{-1}$  along the  $NH$ ,  $N\Gamma$ , and  $NP$  directions, respectively. Our results are 0.229, 0.371, and 0.375  $\text{\AA}^{-1}$ , respectively. The agreement is not good. However, it is not certain that the results should be the same since the size of the pocket could be modified by the establishment of antiferromagnetic order.

#### D. Charge Density

The calculated charge density can be related to experiment through the calculation of the x-ray atomic scattering form factor. This quantity has

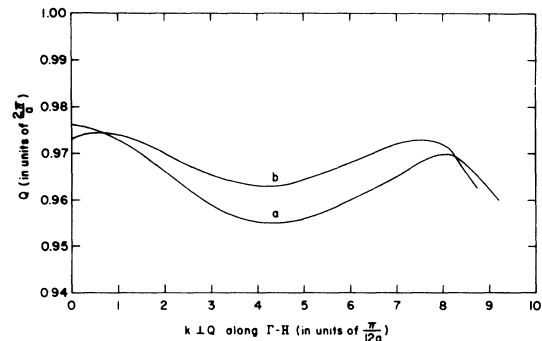


FIG. 5. Variations of the nesting wave vector along the Fermi surface in the two planes perpendicular to the [001] axis. Curve a,  $k_z = 0$ ; curve b,  $k_z = \frac{1}{12} \pi/a$ .

been measured by Diana and Mazzone.<sup>34</sup> Our results are compared with the experimental values in Table IV. The theoretical results tend to be slightly larger than the experimental ones. However, the values given here are in substantially better agreement with experiment than those com-

puted from atomic wave functions and quoted by Diana and Mazzone.

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