Electronic structure and superconductivity of fcc Cr

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Results of self-consistent electronic structure calculations are reported for metastable fcc Cr metal. Unlike the case of bcc Cr which has E_F at a minimum in the density of states (DOS), the DOS at E_F in fcc Cr is at a peak making this one of the higher-DOS metals with the fcc structure (e.g., comparable with that of Ni and Pt). A calculated Stoner factor of 0.82 indicates that ferromagnetic ordering is not expected. Calculations of the electron-phonon coupling parameter λ and superconducting transition temperature T_c were made using the rigid-ion approximation and strong-coupling theory with various estimates of the (unknown) phonon contribution. We conclude that T_c's$\approx$2.5 K are reasonable, although they are substantially smaller than the $T_c \approx 10$ K derived from measurements on Au-Cr-Au sandwiches.

The ability to prepare epitaxial thin films with modified lattice parameters or metastable new crystallographic structures of metals represents a new and exciting area in materials research.[1] Thus, expanded Pd has been prepared with Au or Ag(100) in an epitaxial sandwich form. The combined stretched Pd lattice and tetragonal distortion at the Au-Pd or Ag-Pd interfaces has given rise to a very large enhancement of the susceptibility and perhaps a weak ferromagnetic ordering in the case of Au-Pd-Au (Ref. 1) and to superconductivity in a sample of Ag-Pd-Ag.[2] Most recently, the epitaxial preparation of Cr in Au-Cr-Au sandwiches has been shown to lead to the formation of metastable fcc Cr.[3] Whereas the usual bcc Cr structure gives rise to antiferromagnetism via spin-density-wave formation, sandwiched fcc Cr has been found to be a superconductor. Superconducting transition temperatures (T_c's) up to 3.5 K have been observed, which translate to bulk T_c's greater than 10 K when the Au normal-state proximity effect is considered.[3]

Clearly, the dramatic change in the properties of Cr due to the change in crystal structure is indicative of major changes in the electronic structure of the Cr. This paper presents the first determination of the electronic structure of this new phase, fcc Cr. The calculations were performed using a self-consistent local-density all-electron semirelativistic energy-band approach. As an estimate of a possible magnetic instability, we have also determined the Stoner factor. In view of the superconductivity reported for sandwiched fcc Cr, calculations were also made of the electron-phonon coupling parameter λ and T_c, using various estimates of the phonon contribution in the rigid-ion approximation[4] and strong-coupling theory,[5] respectively.

The energy-band structure was determined by a semirelativistic, self-consistent linearized muffin-tin orbital (LMTO) method.[6] That is, the valence states were treated semirelativistically (all relativistic terms included except spin-orbit coupling) while the core states were treated fully relativistically (spin-orbit coupling included) at each iteration of the calculation. The basis set included s, p, d, and f orbitals, i.e., $l_{\max}=3$. The Hedin-Lundqvist[7] local-density exchange and correlation potential was used.

Although it is to be expected that the results are dependent on the lattice parameter, only one such value was used in this initial study. Thomas and Haas[8] reported $a_0=3.7$ Å for fcc Cr on Au(111), but they did not consider the possibility of a changed inner potential as a function of Cr coverage. (Alternatively, a value of $a_0=3.52$ Å would be estimated for $\Delta a_0/a_0$ of the same magnitude as that found in other bcc-fcc transitions.) Further, the apparent satisfactory lattice match observed for the (100) face of Au could indicate a larger unit cell. The Wigner-Seitz cell sphere radius was chosen as $0.3908a_0=2.7325$ a.u., using the Thomas and Haas[8] value. The band-structure results were obtained using 355 $\vec{k}$ points of the irreducible $\frac{1}{48}$th of the fcc Brillouin zone in the self-consistent iterations. Self-consistency was carried out to 0.001 Ry. The total and partial (l-projected) densities of states (DOS's) were obtained, as was the Fermi energy E_F from a $\vec{k}$-point–weighted histogram scheme.

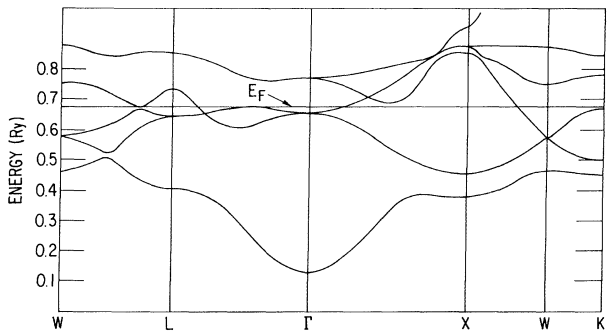

FIG. 1. Calculated band structure for fcc Cr plotted along high-symmetry directions.

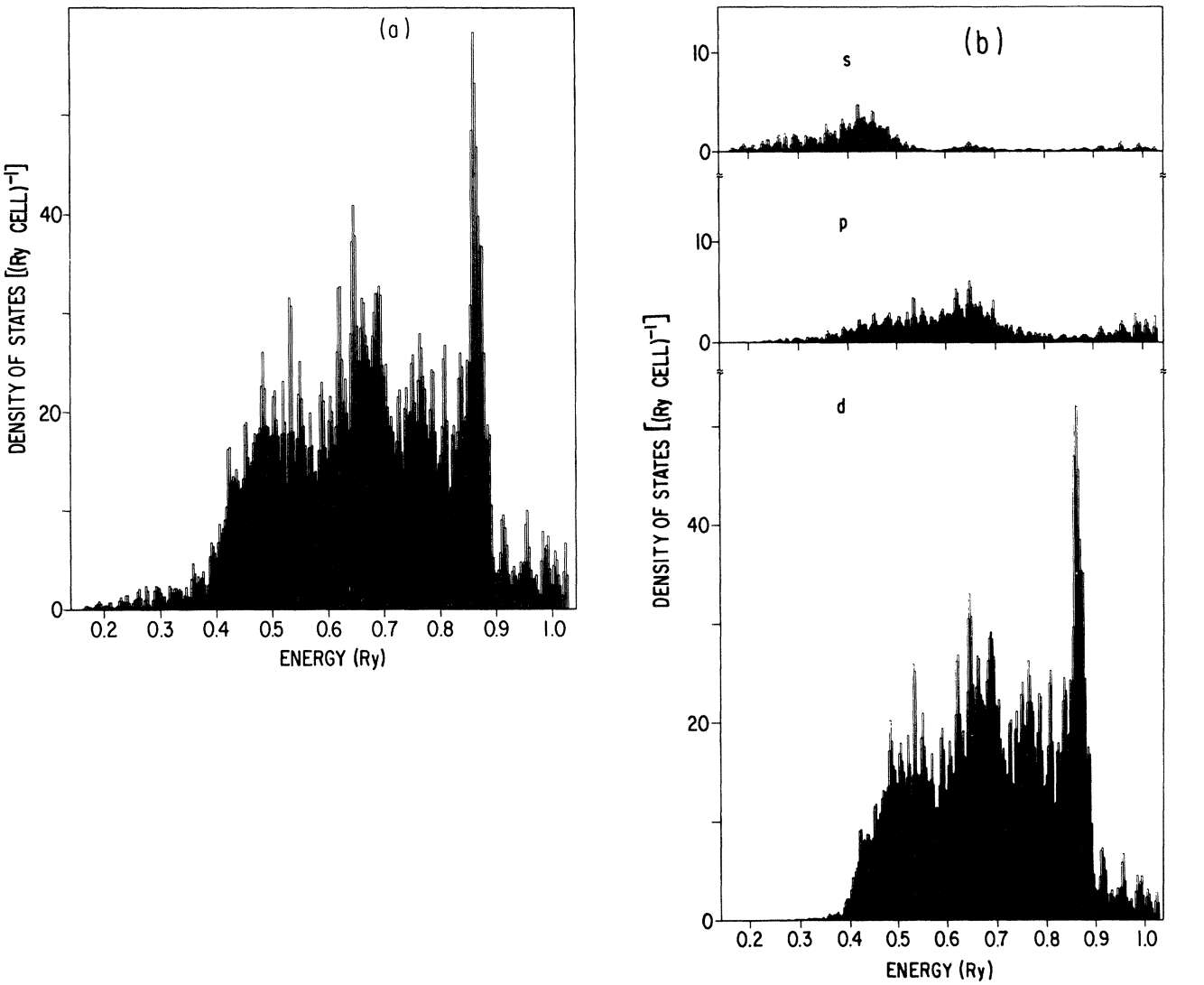

FIG. 2. Calculated DOS: (a) total DOS and (b) by angular-momentum projection.

The calculated band structure is shown in Fig. 1, plotted along the usual high-symmetry directions; it closely resembles the bands of other fcc transition metals. Figure 2 shows the total DOS [Fig. 2(a)] and the angular-momentum-projected DOS [Fig. 2(b)]. The calculated overall structure in the total DOS is found to be very similar to that of a typical fcc $3d$ transition metal such as fcc Ni (cf. Table I). Further, a large value for the total DOS is to be expected from rigid-band extrapolations of the results of Moruzzi *et al.*[9] for fcc Ti (four electrons per atom) or for fcc Co (nine electrons per atom) to six electrons per atom (Cr). However, this extrapolation cannot consider the different a_0's for fcc Ti, Co, or Cr, and in fact leads to a major difference in the location of E_F with respect to the band peak for Ti and Co.

Table I lists the calculated values for various electronic-structure–derived properties. As expected, the major contribution to the DOS arises from the d electrons. Most importantly, as seen in Table I, the DOS at E_F of Cr has changed from having the lowest DOS at E_F in a $3d$ transition metal in the bcc structure to becoming one of the higher-DOS metals in the fcc structure. The calculated value, 30.2 states/Ry cell, is comparable to those of Ni and Pt.

As a result of this high DOS at E_F, we first considered the possibility of magnetic ordering using Stoner theory and local spin-density theory. Since a Stoner factor of

TABLE I. Number of valence electrons (by l value) n_l, projected DOS $N_l(E_F)$ at E_F in states/Ry cell, and normalized exchange-correlation energy integrals (in Ry by l value).

	n_l	$N_l(E_F)$	I_l
s	0.57	0.28	0.046
p	0.79	2.56	0.053
d	4.56	26.93	0.030
f	0.08	0.39	0.080
Total	6.00	30.16	

TABLE II. Calculated electronic contribution η (in eV/Å^2) to λ, the electron-phonon interaction parameter, and the resultant T_c value obtained with $\Theta_D=450$ K.

η	λ	μ^*	T_c
5.50	0.58	0.17_8	2.5

0.82 (or an exchange enhancement of 5.6) was obtained, magnetism is not to be expected. On the other hand, from a DOS consideration alone, T_c's in the range encountered with Nb and V might be expected, depending on the phonon properties of fcc Cr. We have undertaken a calculation of T_c in order to explore whether fcc Cr can have a T_c in the range required to understand the experimental observations.

As of now, no phonon-related properties are known for fcc Cr. The Debye temperature for bcc Cr, $\Theta_D=630$ K, is the highest of all of the 3*d* transition metals. The calculation of T_c was carried out[4,5] for the Debye phonon spectrum first using this very large value of Θ_D and then using $\Theta_D=450$ K, which is the experimental value for fcc Ni. The latter value is more likely to be in the correct range. Table II lists the calculated T_c's.

As expected, even with the high DOS, $\Theta_D=640$ K yields a very low T_c, 0.1 K. However, the more realistic $\Theta_D=450$ K yields $T_c=2.5$ K using a μ^* value (0.17_8) obtained from the Bennemann-Garland[10] formula and the calculated DOS at E_F. The effect of μ_{sp} is nontrivial, also. Whereas, $T_c=2.5$ K was derived with $\mu_{sp}=0.0$, the use of $\mu_{sp}=0.05$ causes T_c to drop by almost half.

In fact, $T_c=2.5$ K is too low for a good fit to the data. Thus, proximity-effect calculations[3] for a sandwich having Au(730 Å)-Cr(11 Å)-Au(730 Å), would require a bulk T_c of 19 K. However, it had been assumed that the 11-Å Cr film may not be perfectly flat. Thus, the thicker regions would determine the measured T_c. An effective film thickness twice the average thickness, or 22 Å, and a bulk T_c of 10 K, fit the data well.

Finally, it should be emphasized that the calculations are made using an approximate lattice constant, an undistorted fcc structure, and assumed (but unknown) values of the phonon properties. Clearly, all are expected to affect the calculated value of T_c. Nevertheless, the present results indicate that superconductivity is likely in pure fcc Cr.

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