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ENERGY BAND STRUCTURE OF Cr
BY THE SLATER-KOSTER INTERPOLATION SCHEME *

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ABSTRACT

The matrix elements of the Hamiltonian between nine localized wave-functions in tight-binding formalism are derived. The symmetry adapted wave-functions and the secular equations are formed by the group theory method for high symmetry points in the Brillouin zone. A set of interaction integrals is chosen on physical ground and fitted via the Slater-Koster interpolation scheme to the abinito band structure of chromium calculated by the Green function method. Then the energy band structure of chromium is interpolated and extrapolated in the Brillouin zone.

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I.   INTRODUCTION

The development of interpolation schemes, which short circuit many of the calculational complexities inherent in energy band structure calculation by the judicious use of symmetry argument and group theory method leads to a deeper understanding of the qualitative features of the electron energy versus wave-number dispersion relation. The Slater-Koster interpolation scheme is used as a useful adjunct of first-principle band Calculation [1], which began with a carefully chosen one-electron potential and are frequently carried out self-consistently. These calculations can be particularly carried out only at few high symmetry points in the Brillouin zone (BZ).

II.   ENERGY BANDS IN Cr VIA THE SLATER-KOSTER INTERPOLATION SCHEME

The energy band structure of Cr was computed at few high symmetry points in the 1/48 part of the BZ (Fig.1) by Green's function method, by S. Asano and J. Yamashita [2]. The Green's function method [3] has merits of yielding quantitatively accurate results. To obtain energy versus wave-vector dispersion relation at all points in the BZ, a more promising approach is to use interpolation scheme. In light of this, the energy band structure of Cr is interpolated and extrapolated in the whole BZ by the Slater-Koster interpolation scheme [4].

Within this framework one has to drive the matrix elements of the Hamiltonian between nine localized wave-functions in tight-binding [5] formalism. The symmetry adapted wave-functions are formed by group theory [6] method for symmetry points and lines of particular symmetry in the BZ. The secular equations [7] for symmetry points and lines are derived using the symmetrized wave-functions as basis set of the group representation. The secular determinant which is in general 9 X 9 and complex is obtained in its reduced form. The interaction integrals involved in the matrix elements of the Hamiltonian are related to one another by judicious use of symmetry arguments and physical insight. Then the matrix elements, thereby the secular equations are expressed in terms of the independent set of interaction integrals. These independent integrals are treated as disposable constants and are fitted to the first-principle energy band structures of Cr via the Slater-Koster interpolation scheme.

Taking contribution from the nearest, second nearest and third nearest neighbours amongst the nine atomic wave-functions, there will be 2106 types of interaction integrals but most of them are dependent. Making use of all the relations which symmetry permits between these integrals only 45 of them are found to be independent.

Amongst the independent interaction integrals 15 of third nearest neighbours integrals are taken to be zero. This is the first natural simplification in the interpolation scheme since the interaction integrals will decrease fairly rapidly as the interatomic distance increases.

The value of the interaction integrals of Cr (Table 1) is determined by a variation procedure using iron interaction integrals [10, 11] as rough initial values since Fe and Cr have the same lattice structure (bcc) and then refined until they reproduce the band structure of Cr. The difference in the interaction integrals of Fe and Cr comes from the fact that the two elements have different atomic potentials. The interaction integrals which are treated as disposable constants in the Slater-Koster interpolation scheme are denoted by

$$E_{nm} (P,q,S) = \int_V \Psi_n(\vec{r}) \hat{H}(\vec{r}) \Psi_m(\vec{r} - Pa\hat{i} - qa\hat{j} - sa\hat{k}) dv$$

The values of these integrals thus obtained apart from being the principal results of this work, may be directly used to compute energy band structures, density of states [8] and the complex energy band structures [9] of Cr. Furthermore, these results can be used for the study of magnetism and also in studying optical properties related to transition between the energy bands.

III. INTERPOLATION AND EXTRAPOLATION OF THE ENERGY BANDS OF Cr

The electronic energy band structures of Cr are computed by using the values of $E(\vec{K})$ computed by the Green function method at few points in the 1/48 part of the BZ. The present computation is carried out at more dense mesh of points than it is done in the first-principle calculation of Asano and Yamashita [2].

The computations have been carried out at high symmetry points Γ, P, N, H and along the symmetry lines Δ, Λ, Σ, D and also along a low symmetry line from symmetry point P to point X in the BZ. The energy band structures interpolated along symmetry lines by the Slater-Koster interpolation scheme are shown in Figures (2 to 5) together with the corresponding points computed by the Green's function method [2].

Our energy band structure of Cr was computed even for higher energy levels (that is $\xi > 0$ Ry) that are not given by the first-principle method. This is basically one of the advantages of the Slater-Koster method which makes it also an extrapolation scheme. The obvious achievement of this method pertains to the interpolation of the energy band structure along any general direction in the BZ which is not computed by the first-principle method. As an illustration energy bands along a general direction are shown in Fig 6. This involves solving 9X9 complex secular equation at all points along this direction for it lacks symmetry the secular determinant does not have reduced form. The only operator which leaves this direction invariant is the identity operator.

IV. DISCUSSION

In Fig. 3 the higher bands along Λ-direction Λ_1 at $\vec{K} \approx <\frac{\pi}{8a} \frac{\pi}{8a} \frac{\pi}{8a}>$ and along Σ-direction Σ_1 at $\vec{K} = <\frac{\pi}{4a} \frac{\pi}{4a} 0>$ show some anomally. There is also a sharp peak in the energy band along D-direction D_3 at $\vec{K} = <\frac{\pi}{2a} \frac{\pi}{2a} \frac{3\pi}{8a}>$ (Fig.4) and the higher band along the symmetry direction D^+ show some anomally at $\vec{K} = <\frac{\pi}{16a} \frac{\pi}{2a} \frac{3\pi}{16a}>$.

One of the reasons that the unexpected peaks occurring in the higher bands is due to the fact that the energy values for higher bands is not calculated by the first-principle method. So, in the processes of improving the values of the parameters by our variational procedure, the secular equations

for higher bands were disregarded due to the deficient available data and this produces an abnormal behaviour in the higher bands. The other important reason that accounts for the observed anomaly is the neglect of some of the inter-action integrals between the third nearest neighbours.

Some discrepancy is also seen in the interpolated bands. The maximum error, that is the maximum difference between energy values calculated by the first-principle method and the interpolation scheme is 0.08459 Ry and it is along the Λ-direction Λ_1- band at $K = \langle \frac{\pi}{8a} \frac{\pi}{8a} \frac{\pi}{8a} \rangle$.

These discrepancies reflect shortcomings of the method when it is used as a quantitative method of determining energy bands. The reason for this is not far to seek. The Slater-Koster interpolation scheme which is basically LCAO method regarded as a mathematical method of obtaining appro-ximate solutions of the Schroedinger equation, is most successful when the interatomic distance of a nearest neigh-bours is large compared with the spread of the atomic wave-functions.

Since the $\vec{K}$ - vector along the Λ - direction intersects perpendicularly the <111> plane on which the number of atoms is relatively less and therefore the interatomic distance is shorter compared to the spread of atomic wave-functions, the maximum discrepancy is observed between energy values along the Λ - direction for the LCAO method met its limitation along this direction.

On the other hand this method is at its best along the Σ - direction. The $\vec{K}$ - vector along the Σ - direction intersects perpendicularly the <110> plane which is the most dense plane in bcc lattice. The separation between planes along this direction is relatively longer to preserve the number of particles in a primitive unit cell of the Bravais lattice. Hence, the LCAO method is most successful along this direction for the interatomic distance of nearest neigh-bours is large compared with the spread of the atomic wave-functions.

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Table 1. Values of the Interaction Integrals for Chromium in Rydberg Units

$E_{11}(000) = 0.3401$	$E_{99}(111) = 0.0238$
$E_{22}(000) = 0.5240$	$E_{11}(200) = -0.0291$
$E_{55}(000) = -0.2548$	$E_{12}(200) = 0.1128$
$E_{99}(000) = -0.2536$	$E_{19}(002) = -0.0169$
$E_{11}(111) = -0.1341E$	$E_{22}(200) = 0.1698$
$E_{12}(111) = 0.9665$	$E_{33}(200) = 0.0315$
$E_{15}(111) = -0.0387$	$E_{25}(020) = 0.0193$
$E_{22}(111) = 0.0941$	$E_{49}(002) = -0.0296$
$E_{23}(111) = 0.0365$	$E_{55}(200) = 0.0154$
$E_{25}(111) = 0.0154$	$E_{55}(002) = 0.0030$
$E_{27}(111) = -0.0224$	$E_{88}(002) = -0.0009$
$E_{28}(111) = 0.0256$	$E_{99}(002) = -0.0418$
$E_{55}(111) = -0.0151$	$E_{11}(220) = 0.0119$
$E_{56}(111) = -0.0229$	$E_{15}(220) = -0.0061$
$E_{59}(111) = -0.0201$	$E_{55}(220) = -0.0040$
	$E_{59}(220) = 0.0005$

Fig.1   The 1/48 part of Brillouin zone faces showing the points
          at which $E(\vec{k})$-values are computed by the Green function
          method.

Fig.2 $E(k)$-values of Cr along Δ-direction in BZ. $E(\vec{k})$ values
          computed by the Slater-Koster interpolation scheme
          (denoted by "x")together with the corresponding $E(\vec{k})$-
          values calculated by the Green function method (denoted
          by "o").

Fig.3 $E(k)$-values of Cr along the Σ and Λ-direction in BZ. Same as
          Fig.2.

Fig.4 $E(k)$values of Cr along the D-direction and P-X-direction in
          BZ. Same as Fig.2.

Fig.5. $E(k)$-values of Cr along G and F-direction in BZ. Same as Fig.2.

Fig.6 $E(\vec{k})$-values of Cr in units of Rydberg computed by the Slater-
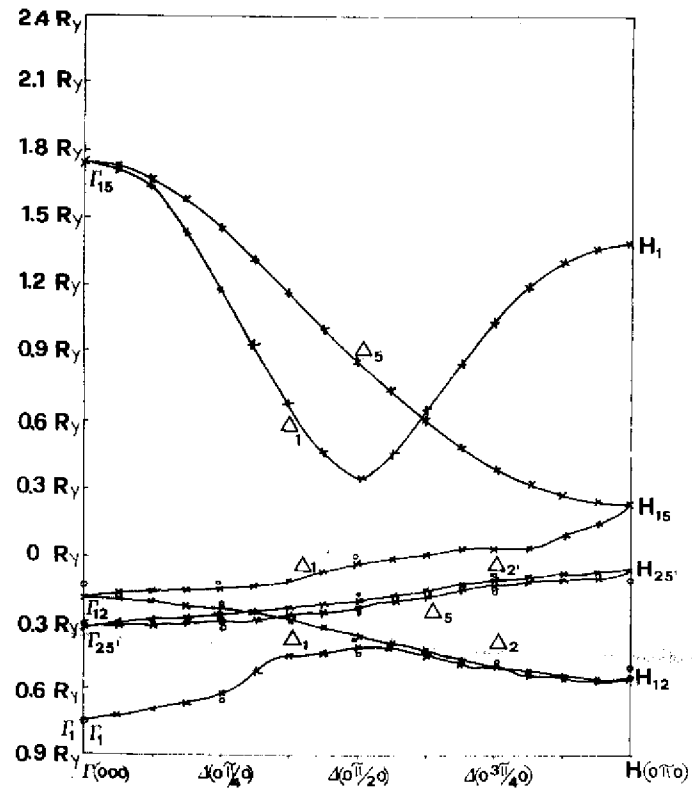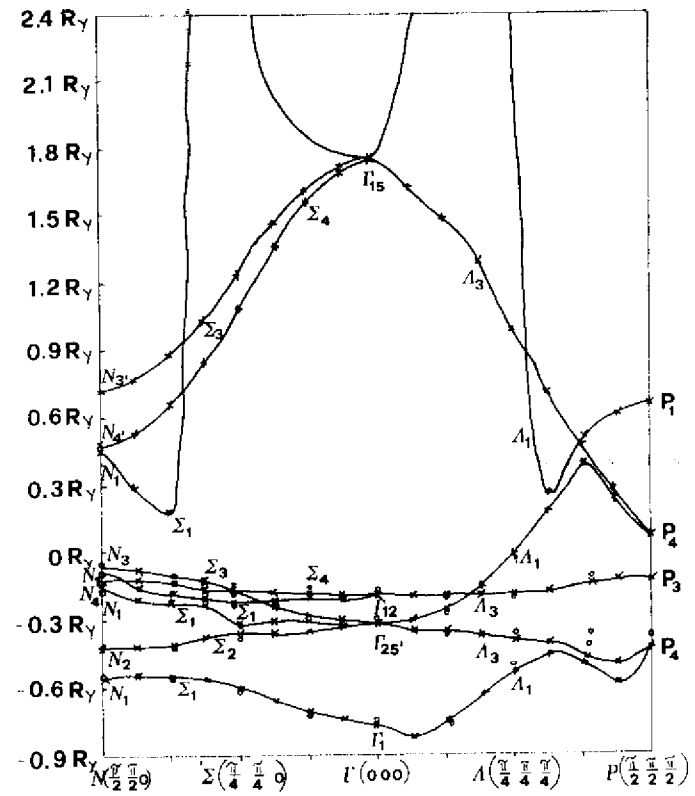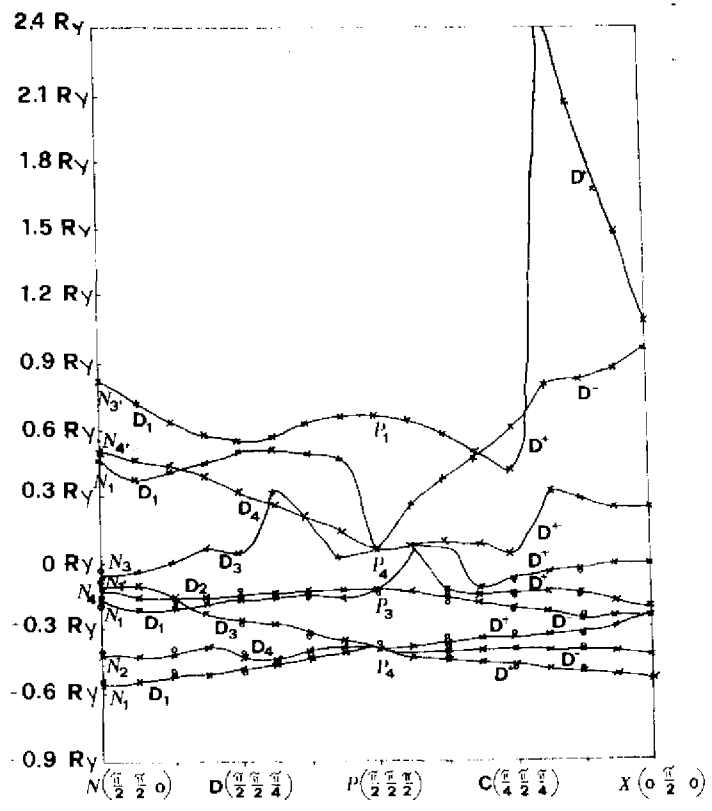   Koster interpolation scheme along a general direction in BZ.
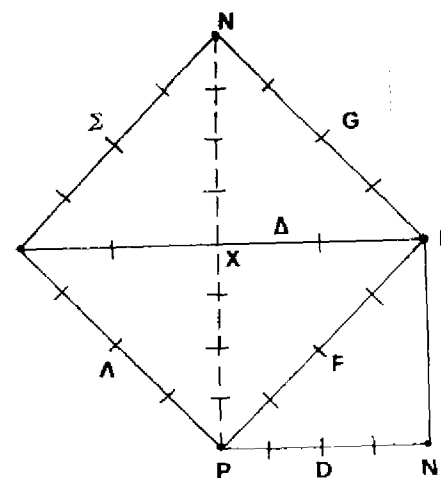
Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6