

## Electronic Band Structure of $\alpha$ -Brass

M. M. PANT AND S. K. JOSHI

*Physics Department, University of Roorkee, Roorkee, India*

(Received 26 December 1968)

The Kohn-Rostoker method has been used to determine the energy bands, within the virtual-crystal approximation, of  $\alpha$ -brass. The conduction-band energies have been determined at the points  $\Gamma$ ,  $X$ , and  $L$  for a range of zinc concentrations. The averaged effective potential to be placed at the lattice sites of the equivalent crystal is computed from realistic considerations, and results are compared with experiments and other theoretical results. Discrepancies between computed and experimental values reflect the inadequacies of the virtual-crystal model.

### I. INTRODUCTION

THE existing theories of the electronic structure of disordered alloys are in a very primitive stage compared with those for pure metals. The theoretical work in the latter field was greatly stimulated by the large amount of experimental data available. Most of the experimental techniques employed in obtaining detailed information about the Fermi surface in ordered materials require the existence of long electron relaxation times, and are, therefore, inappropriate for the study of nondilute alloys. Nonetheless, rapidly deepening understanding of alloys is being gained by a steady increase in data from optical studies. The development of positron annihilation techniques has opened a new vista towards the delineation of the Fermi surface in alloys. This method has recently been applied to determine the Fermi surface of copper-aluminum alloys.<sup>1</sup>

Progress is now being made towards the understanding of the electronic states of alloys. The averaged  $t$ -matrix approximation, introduced by Korringa<sup>2</sup> and developed by Beeby,<sup>3</sup> was cast by Soven<sup>4</sup> into a form amenable to computation. Soven applied the theory to  $\alpha$ -brass. In a later application to a model one-dimensional alloy, Soven<sup>5</sup> finds that a "coherent potential model," which modifies the electron Green's function and determines the modified Green's function in a self-consistent way, provides a more reasonable facsimile of the density of states. The extension of this calculation to three dimensions has not yet been possible. A formal approach to the problem of electronic states in alloys has been adopted by Yonezawa and Matsubara,<sup>6</sup> who sum a selected class of terms in a perturbation series of the alloy Green's function. However, no actual calculations have been reported along these lines for a real alloy.

Amar, Johnson, and Sommers<sup>7</sup> (AJS) adopted the "virtual-crystal approximation" in order to investigate the band structure of noble-metal alloys. In this approximation, the actual potential appropriate to a particular arrangement is replaced by its mean value over all possible random arrangements. The disordered crystal is thus replaced by an equivalent ordered crystal with each lattice site carrying a potential  $\langle V(\mathbf{r}) \rangle_{av}$ .

We present here the results of an energy-band calculation for  $\alpha$ -brass, within the framework of the virtual-crystal approximation, using the Kohn-Rostoker (KR) method.<sup>8</sup> Our choice of  $\alpha$ -brass was dictated by the availability of experimental data<sup>9</sup> and by the fact that the electron spectrum of the host lattice is well understood.

In their calculations for  $\alpha$ -brass, AJS postulate that the "effective potential" to be used in the virtual-crystal model is given by

$$\langle V(\mathbf{r}) \rangle_{av} = (1-c)V_A(\mathbf{r}) + cV_B(\mathbf{r}), \quad (1)$$

where  $V_A(\mathbf{r})$  and  $V_B(\mathbf{r})$  are the atomic potentials<sup>10</sup> for copper and zinc and  $c$  is the zinc concentration. Their results are in close agreement with Biondi and Rayne's<sup>9</sup> experimental results. This agreement, however, appears to be fortuitous in view of the fact that, for copper, Ballinger and Marshall<sup>11</sup> find that the atomic potential did not give an over-all satisfactory representation of the energy bands. Therefore, AJS had to adjust their bands for 0% Zn, in order to make them agree with Segall's<sup>12</sup> results for pure copper.

The present work seeks to assess the intrinsic worth of the virtual-crystal model by making a better approximation to  $\langle V(\mathbf{r}) \rangle_{av}$  and comparing the resulting bands with those obtained from experiments. Besides being a better approximation to the alloy potential, this has the advantage that no adjustments of the bands are necessary for 0% Zn. The average potential  $\langle V(\mathbf{r}) \rangle_{av}$  is

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<sup>2</sup> J. Korringa, *J. Phys. Chem. Solids* **7**, 252 (1958).

<sup>3</sup> J. L. Beeby, *Phys. Rev.* **135**, A130 (1964).

<sup>4</sup> P. Soven, *Phys. Rev.* **151**, 539 (1966).

<sup>5</sup> P. Soven, *Phys. Rev.* **156**, 809 (1967).

<sup>6</sup> F. Yonezawa, *Progr. Theoret. Phys. (Kyoto)* **31**, 357 (1964); F. Yonezawa and T. Matsubara *ibid.* **35**, 357 (1966); **35**, 759 (1966).

<sup>7</sup> H. Amar, K. H. Johnson, and C. B. Sommers, *Phys. Rev.* **153**, 655 (1967).

<sup>8</sup> W. Kohn and N. Rostoker, *Phys. Rev.* **94**, 1111 (1954).

<sup>9</sup> M. A. Biondi and J. A. Rayne, *Phys. Rev.* **115**, 1522 (1959).

<sup>10</sup> F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall Inc., Englewood Cliffs, N. J., 1963).

<sup>11</sup> R. A. Ballinger and C. A. W. Marshall, *Proc. Phys. Soc. (London)* **91**, 203 (1967).

<sup>12</sup> B. Segall, *Phys. Rev.* **125**, 109 (1962).

TABLE I. Conduction-band energies and level separations (in Ry) for  $\alpha$ -CuZn (with Heine-type potentials) over a 0–30% range of Zn concentrations.

	0%	5%	10%	15%	20%	25%	30%
$\Gamma_1$	-0.256	-0.298	-0.339	-0.382	-0.426	-0.469	-0.515
$X_{4'}$	0.881	0.822	0.776	0.708	0.652	0.596	0.540
$X_1$	0.541	0.489	0.444	0.397	0.348	0.301	0.255
$L_{2'}$	0.305	0.259	0.212	0.165	0.120	0.076	0.026
$L_1$	0.672	0.610	0.544	0.477	0.419	0.364	0.299
$L_1-L_{2'}$	0.367	0.351	0.332	0.312	0.299	0.288	0.273

then simply an appropriate crystal potential for pure copper.

The conduction-band states at the symmetry points  $\Gamma$ ,  $X$ , and  $L$  were computed using the KR method when the zinc concentration varied from 0 to 30% at intervals of 5%. The more tightly bound  $3d$  electrons of copper have been assumed to remain unaffected by the changes in potential induced by the substitution of zinc atoms. Within this limited calculation, the Fermi energy is determined on the basis of the simple approach suggested by Cohen and Heine.<sup>13</sup>

The KR method is particularly suited for this kind of an investigation on account of the following reasons.

(a) The rapid convergence of the KR method, together with the use of symmetry considerations in choosing the basis functions, results in a  $2 \times 2$  determinant being the largest secular determinant in the present work.

(b) The bulk of the computation is involved in evaluating the structure constants, which need to be calculated once and for all. The effect of changing the zinc concentration is then simply to change the effective potential, which enters the secular determinant through the logarithmic derivatives of the radial wave functions at the “muffin-tin” spheres. Calculating these is a relatively simple matter.

## II. POTENTIALS

### A. Heine Potential

This class of potentials is often used for orthogonalized-plane-wave (OPW) calculations of normal metals and is obtained as a sum of several individual contributions of the core and conduction electrons, computed according to the method first suggested by Heine.<sup>14</sup> The potentials for copper and zinc are constructed in this manner and used for  $V_A(r)$  and  $V_B(r)$ , Eq. (1).

The Wigner-Seitz cell is assumed to consist of a positive-ion core, embedded in a uniform distribution of negative charge to make the cell neutral. We have evaluated the core contribution as the sum of the Coulomb contribution of the core plus a screened Slater

exchange.<sup>15</sup> The conduction-electron contribution was determined as the Coulomb contribution of a charge uniformly distributed within the Wigner-Seitz cell. Exchange and correlation between core and conduction electrons is accounted for, according to the approach by Robinson *et al.*<sup>15</sup> *Prima facie*, the above scheme seems to be a better approximation to the crystal potential than would be the atomic potential. However, when we consider the fact that, for copper, the classification into core and conduction-band states is not quite natural, it appears that any advantage gained by such detailed considerations may be offset by the difficulty of defining the “core.”

If we assume that a copper cell is represented by a  $\text{Cu}^+$  ion within a uniform distribution of unit negative charge, and a zinc cell by  $\text{Zn}^{++}$  within a distribution of two electrons, the potential for Cu in  $\alpha$ -brass is found to be deeper than that for Zn. This seems unreasonable and causes the bands to be pushed up with increasing zinc concentration, contrary to the results of Soven and of AJS. The prescription was, therefore, deemed unreasonable, and we assume a uniform distribution of one electron in all the cells and treat the cores as  $\text{Cu}^+$  and  $\text{Zn}^+$ . This is consistent with Friedel’s proposal<sup>16</sup> that the excess charge on the nucleus of the solute is locally screened out by the excess electronic charge. The potential for zinc is then very much deeper than that for copper, and the bands are pulled down to a much greater extent than calculated by AJS. The energy values for this potential are listed in Table I. There is a general downward displacement of the levels as the zinc concentration is increased. The displacement of  $L_1$  is somewhat greater than that of  $L_{2'}$ , resulting in a reduced  $L_{2'}-L_1$  gap. The computed decrease for 30% Zn is found to be 1.278 eV, compared with the experimentally observed<sup>9</sup> value of 1.3 eV. AJS also find a value of 1.3 eV for the reduction in this gap. The upward shift of the Fermi level above  $L_{2'}$  for 30% Zn is found to be 0.952 eV, compared with the value of 1.84 eV obtained by AJS.

### B. Superposed Atomic Potentials

The type of crystal potential which has been found to be most successful in describing the band structure of transition and noble metals is obtained from a super-

<sup>13</sup> M. H. Cohen and V. Heine, *Advan. Phys.* **7**, 395 (1958).

<sup>14</sup> V. Heine, *Proc. Roy. Soc. (London)* **A240**, 340 (1957); **A240**, 354 (1957); **A240**, 361 (1957).

<sup>15</sup> J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, *Phys. Rev. Letters* **9**, 215 (1962).

<sup>16</sup> J. Friedel, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1958), Vol. 3, p. 461.

TABLE II. Energy values and level separations (in Ry) for the conduction bands in  $\alpha$ -CuZn with overlapped potentials, (Cu potential  $V_I$ ) for a range of Zn concentrations.

	0%	5%	10%	15%	20%	25%	30%
$\Gamma_1$	-1.479	-1.477	-1.475	-1.473	-1.472	-1.4703	-1.4702
$X_4'$	-0.694	-0.6916	-1.6912	-0.6907	-0.6895	-0.6892	-0.6890
$X_1$	-0.4002	-0.4015	-0.4020	-0.4041	-0.4046	-0.4050	-0.4064
$L_2'$	-0.9256	-0.9244	-0.9232	-0.9219	-0.9207	-0.9190	-0.9164
$L_1$	-0.6354	-0.6359	-0.6372	-0.6376	-0.6381	-0.6396	-0.6407
$L_1-L_2'$	0.2902	0.2885	0.2860	0.2843	0.2826	0.2794	0.2757

position of atomic potentials on neighboring sites.<sup>17</sup> The crystal potential is represented as the sum of a Coulomb and an exchange part, both being obtained from atomic wave functions. At any lattice point the Coulomb part is taken to be the Coulomb potential located at that site plus contributions from neighboring sites. This is evaluated by employing Lowdin's  $\alpha$ -function expansion technique and retaining only the spherically symmetric term as implied in the muffin-tin approximation. The crystal charge density is obtained by a spherically symmetric superposition of the atomic charge densities in an analogous manner. The exchange potential is calculated from Slater's formula.

Mattheiss<sup>18</sup> has shown that this prescription generates a potential which gives a satisfactory representation of the band structure for the iron-transition series. However, the work of Davis *et al.*<sup>19</sup> on Cu reveals that the details of the band structure are very sensitive to the choice of atomic charge densities employed in the calculation. Examining three different sets of atomic wave functions for Cu, they conclude that best results are obtained for the potential constructed for an assumed  $3d^{10}4s^1$  configuration using the atomic wave functions of Watson<sup>20</sup> for a  $3d^9 4s^2$  configuration. This can be understood in terms of the  $s$ - $d$  hybridizations in noble metals. Since our intention here is to use realistic crystal potentials for the alloy constituents, we have calculated the Cu potential from atomic charge densities for a  $3d^{10}4s^1$  configuration using wave functions generated by the Herman-Skillman program<sup>10</sup> for a  $3d^9 4s^2$  configuration. This potential will be referred to as  $V_I$ . We have also performed calculations using a potential  $V_{II}$  derived from a  $3d^{10}4s^1$  configuration

throughout. Davis *et al.* find that  $V_I$  is more satisfactory than  $V_{II}$  for pure copper.

The behavior of Zn is known to be significantly free-electron-like, and there is no admixture of core and conduction states. We, therefore, employ wave functions for a  $3d^{10}4s^2$  configuration. Mattheiss<sup>18</sup> obtains quite satisfactory agreement with experiments by using such a potential in an augmented-plane-wave (APW) band calculation for pure Zn.

The virtual potential for the equivalent ordered crystal is taken to be

$$\langle V(\mathbf{r}) \rangle_{av} = (1-c)\langle V_A(\mathbf{r}) \rangle_{av} + c\langle V_B(\mathbf{r}) \rangle_{av}. \quad (2)$$

We use the symbols  $A$  and  $B$  for the solvent and solute, respectively, and  $\langle V_A(\mathbf{r}) \rangle_{av}$  or  $\langle V_B(\mathbf{r}) \rangle_{av}$  is the average potential for an  $A$  or  $B$  atom for the given alloy configuration. The probability that, if a given site is occupied by an  $A$  atom, then a site which is its  $i$ th neighbor will be occupied by a  $B$  atom is denoted as  $P[A|B(i)]$ . If  $\mathbf{r}_\alpha$  locates the various lattice sites referred to the  $A$  site under consideration as origin, then the potential at a point  $\mathbf{r}$  with respect to the  $A$  site is, on the average,

$$\langle V_A(\mathbf{r}) \rangle_{av} = V_A(\mathbf{r}) + \sum_{\alpha} \{ P[A|A(i)]V_A(|\mathbf{r}-\mathbf{r}_\alpha|) + P[A|B(i)]V_B(|\mathbf{r}-\mathbf{r}_\alpha|) \}, \quad (3)$$

where  $V_A(\mathbf{r})$  and  $V_B(\mathbf{r})$  are the potentials of the constituents. This sort of superposition is done along the lines of the Mattheiss prescription involving a separate overlap of the Coulomb potential and the charge

TABLE III. Energy values and level separations (in Ry) for the conduction bands in  $\alpha$ -CuZn with overlapped potentials, (Cu potential  $V_{II}$ ) for a range of Zn concentrations.

	0%	5%	10%	15%	20%	25%	30%
$\Gamma_1$	-1.297	-1.304	-1.301	-1.317	-1.325	-1.331	-1.338
$X_4'$	-0.495	-0.505	-0.514	-0.523	-0.533	-0.542	-0.551
$X_1$	-0.124	-0.140	-0.155	-0.172	-0.187	-0.203	-0.218
$L_2'$	-0.729	-0.739	-0.749	-0.758	-0.769	-0.779	-0.791
$L_1$	-0.350	-0.367	-0.384	-0.400	-0.417	-0.432	-0.448
$L_1-L_2'$	0.379	0.371	0.362	0.355	0.347	0.340	0.334

<sup>17</sup> L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).

<sup>18</sup> L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

<sup>19</sup> H. L. Davis, J. S. Faulkner, and H. W. Joy, Phys. Rev. **167**, 601 (1968).

<sup>20</sup> R. E. Watson, Phys. Rev. **119**, 1934 (1960).

TABLE IV. Comparison of experimental and theoretical results for the level shifts and changes in energy gaps (in Ry) from Cu to  $\alpha$ -Cu<sub>0.70</sub>Zn<sub>0.30</sub>.

	$\Delta X_4'$	$\Delta L_{2'}$	$\Delta L_1$	$\Delta(L_1-L_{2'})$	$\Delta(E_f-L_{2'})$	$\Delta(E_f-L_3)$
Experiment: Biondi and Rayne				0.096		0.026
Theoretical:						
AJS	0.051	0.043	0.139	0.094	0.135	0.035
Soven	0.050	0.045	0.058	0.013	0.825	0.062
Present calc.:						
$V_I$	-0.006	-0.009	0.0053	0.015	0.099	0.0504
$V_{II}$	0.056	0.062	0.098	0.045	0.120	0.1083

density. The exchange potential is calculated from Slater's approximation using the overlapped charge density. The difference from the procedure for pure metals is that the overlap contribution of the  $i$ th neighboring  $A$  (or  $B$ ) atom has to be multiplied by the probability of its occurrence. Otherwise the procedure is similar to the Mattheiss prescription. The  $P$ 's can be related to the short-range order parameters of a disordered alloy.<sup>21</sup> For  $\alpha$ -brass, however, neutron diffraction experiments do not show the presence of any short-range order.<sup>22</sup> The pair-correlation factors  $P[A|B(i)]$  and  $P[A|A(i)]$  are then simply equal to  $c$  and  $1-c$ , respectively, independent of the neighborhood. Potentials constructed from this prescription are more soundly based than the potentials used by AJS. The disparity with experimental results should now reflect mainly the weakness of the virtual-crystal model and not the inadequacies of the potentials of the constituents.

The results for this scheme and employing  $V_I$  for the Cu potential are shown in Table II. Table III shows the results with  $V_{II}$  as the Cu potential. It is seen that the potential  $V_I$  for Cu leads to the surprising result that the levels  $\Gamma_1$ ,  $X_4'$ , and  $L_{2'}$  shift slightly upwards with increasing Zn concentrations but the  $L_1$  and  $X_1$  levels are pulled down. The net effect is that the  $L_{2'}-L_1$  gap is reduced. The computed reduction for 30% Zn compares well with Soven's results but does not agree with the experimental results. For the other potential  $V_{II}$  all the levels are pushed downwards with increasing Zn concentration.

### III. DISCUSSION

The optical properties of  $\alpha$ -brasses over a range of 0–30% Zn concentration has been measured by Biondi and Rayne and interpreted by Lettington<sup>23</sup> in terms of band calculations for pure Cu. It was observed that the 2.2-eV absorption edge in Cu, which is due to transitions between the  $d$  band and the Fermi level near  $L_{2'}$ , shifts to 2.6 eV at  $\alpha$ -Cu<sub>0.70</sub>Zn<sub>0.30</sub>. The secondary absorption peak at 4.2 eV in pure Cu shifts to lower energies, the reduction being 1.3 eV for 30% Zn. This secondary peak at 4.2 eV is attributed to transitions

between the doubly degenerate  $d$  state  $X_5$  and the  $p$  state  $X_4'$ . Transitions across the  $L_{2'}-L_1$  gap are also associated with this edge.

In Table IV, we compare the changes in these level separations for the present calculations using copper potentials  $V_I$  and  $V_{II}$  with experimental and other theoretical results. If the  $d$  bands are assumed to be unaffected upon alloying, the shift in the secondary absorption peak is given by the downward displacement of the  $X_4'$  level. It is seen that for  $V_{II}$  the shift is in fair agreement with both Soven's and the AJS results, but in marked disagreement with the experimentally observed shifts. The displacement of the Fermi level with respect to the  $d$  band for  $V_{II}$  is about twice the experimental value, and lies in between those calculated by Soven and by AJS.

In their calculations, AJS used the structure constants tabulated by Segall and Ham<sup>24</sup>; the corresponding errors in interpolating the secular determinant are estimated at  $\pm 0.01$  Ry. This magnitude of error is too large since the observed reduction in the  $L_{2'}-L_1$  gap is of the order of 0.03 Ry. We have, therefore, evaluated the structure constants at  $\frac{1}{10}$  the energy intervals of Segall and Ham. The corresponding interpolation errors should be  $\pm 0.001$  Ry.

We see that for both potentials  $V_I$  and  $V_{II}$ , the agreement with experimental data is poor. The potentials used in our calculation have been obtained from a prescription proven to be successful in describing the band structure of pure metals. We can therefore attribute the discrepancy with experiments to the inadequacies of the virtual-crystal model.

It is concluded that though the virtual-crystal approximation gives a qualitative picture of the electronic states for  $\alpha$ -brass; it fails to produce quantitative agreement with experimental results.

### ACKNOWLEDGMENTS

The authors acknowledge financial support from the Council of Scientific and Industrial Research, India. We are thankful to the Tata Institute of Fundamental Research, Bombay, for allowing us the use of their computer facilities.

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<sup>22</sup> D. T. Keating, Acta Met. **2**, 885 (1954).

<sup>23</sup> A. H. Lettington, Phil. Mag. **11**, 863 (1965).

<sup>24</sup> B. Segall and F. S. Ham, General Electric Research Laboratory Report, Schenectady, N. Y., No. 61-RL-(2876G), 1961 (unpublished).