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Green's-Function Method for Energy Bands in Disordered Alloys. II. Band Structure of Disordered Cu_3Au

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A generalization of the Green's-function method (proposed by the authors in a previous paper) has been used to determine the energy bands of disordered Cu_3Au. Energies have been calculated at the symmetry points Γ, X, and L for a series of temperatures above the transition temperature. The crystal potentials and the structure constants are calculated using the short-range-order parameters from the available x-ray data. The results are discussed in terms of the available experimental information for this alloy.

I. INTRODUCTION

IN a previous paper[1] (to be referred to hereafter as I), a scheme was suggested for calculating the band structure of disordered alloys. The method was applied to α brass, and was found to give a fairly satisfactory description of both the conduction and the d bands. The choice of α brass was made because of considerable simplification in the computational aspects resulting from the absence of the short-range order.[2] The pair correlation functions, then, become independent of the order of the neighborhood and the structure constants for a disordered lattice are related by simple factors to those of a perfect lattice.

The present paper deals with an application of the above method to a system which is well known for exhibiting the short-range order effects. The alloy Cu_3Au is a classical example of one undergoing the order-disorder transformation. For the perfectly ordered state, all Au atoms are at the cube corners and Cu atoms at the face centers of a cubic lattice. Above the critical temperature of 390°C there is no long-range ordering present. In this case all lattice sites may be occupied by either Au or Cu atoms, but there is a preference in the kind of neighbors about each atom, and this departure from randomness is called the short-range order. Both the x-ray and electron-diffraction methods have been used to study the variation of the short-range order with temperature in this system.[3–5]

Many physical properties of this alloy have been experimentally measured both in the ordered and disordered states. The Hall coefficient was found to be negative for the disordered alloy, but becomes positive for the ordered phase.[6] However, the variation of the Hall coefficient with the short-range order was small. Airoldi and co-workers have carried out measurements of the magnetic susceptibility as well as the thermoelectric power for Cu_3Au as a function of the short-range order.[7] They conclude that the electronic structure and the Fermi surface (if we may use the term) for Cu_3Au in the disordered state are quite similar to those of pure Cu. The specific-heat measurements by Rayne[8] failed to detect a difference in the density of states at the Fermi surface, between the ordered and disordered state. Recent and more refined experiments do show a variation of 3.5% with the setting in of order.[9] The soft x-ray emission spectroscopy shows that the spectrum for this alloy is almost identical with the spectrum of pure Cu. Besides, there is no detectable difference between the emission spectra from the alloy in the ordered and disordered conditions.[10] The positron-annihilation experiments by Dekhtyar *et al.* revealed the maximum conduction-electron momentum to be the same for the ordered and disordered Cu_3Au.[11] Very recently, both the ordered and disordered Cu_3Au have been studied by the optical and photoemission techniques, and the imaginary part of the dielectric constant has been obtained from a Kramers-Kronig analysis of the data. The spectrum of the disordered sample was found to be well represented by a superposition of the spectra of the pure constituents.[12]

All these properties cannot be interpreted in terms of the band structure alone. Still, we thought it would be interesting to investigate the dependence of the band structure of the disordered Cu_3Au, on the degree of the short-range order. Fairly detailed calculations of the energy bands have already been carried out for the ordered Cu_3Au by Gray and Brown.[13] They employed the modified-plane-wave method in conjunction with the orthogonalized-plane-wave method. The crystal potential was constructed by slightly modifying the atomic potentials of Herman and Skillman.[14]

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II. EVALUATION OF THE STRUCTURE CONSTANTS

The method adopted in this calculation has been described in detail in I, and we recount here the chief steps, with emphasis on the calculation of the structure constants. The energy values are given by the zeros of the secular determinant Eq. (I18).[15]

$$|B_{LL'}{}^{ss'}+\kappa \cot\eta_l{}^{(s)}\delta_{ll'}\delta_{ss'}|\,. \qquad (1)$$

The $B_{LL'}{}^{ss'}$ occur as coefficients in the expansion of the incomplete Greenians, defined in I. The incomplete Greenians are given by the expression

$$G^{ss'}(\mathbf{R})=-\frac{1}{4\pi}\sum_{\alpha}\frac{\exp(i\kappa|\mathbf{R}-\mathbf{r}_\alpha|)}{|\mathbf{R}-\mathbf{r}_\alpha|}\times\exp(i\mathbf{k}\cdot\mathbf{r}_\alpha)P^{ss'}(\mathbf{r}_\alpha)\,, \qquad (2)$$

where the summation is over all lattice sites and $P^{ss'}(\mathbf{r}_\alpha)$ is the probability of finding an s'th type atom at a position $\mathbf{r}_\alpha$ with respect to an atom of sth type. This probability may be calculated from the experimentally determined short-range order parameters, as discussed in I. In the case of a perfect lattice, all the $P^{ss'}(\mathbf{r}_\alpha)$ are unity, and Ham and Segall[16] have shown how the Ewald procedure may be used to transform the Green's function into a rapidly convergent sum. For a disordered crystal, the presence of $P^{ss'}(\mathbf{r}_\alpha)$ does not allow us to follow such an approach. Therefore, we assume that the short-range order extends only through a neighborhood σ beyond which it is significantly zero. That is, beyond σ the occupation probabilities are constant—corresponding to the completely random occupation of the lattice sites. We call σ *the order of the significant neighborhood.* If $G(\mathbf{R})$ denotes the complete Greenian for the perfect lattice, we have

$$G^{ss'}(\mathbf{R})=P_R{}^{ss'}G(\mathbf{R})-\sum_{\alpha<\sigma}\frac{\exp(i\kappa|\mathbf{R}-\mathbf{r}_\alpha|)}{|\mathbf{R}-\mathbf{r}_\alpha|}\exp(i\mathbf{k}\cdot\mathbf{r}_\alpha)\times[P^{ss'}(\mathbf{r}_\alpha)-P_R{}^{ss'}]\,, \qquad (3)$$

where $P_R{}^{ss'}$ is the limiting value of $P^{ss'}(\mathbf{r}_\alpha)$ in the absence of the short-range order. We may expand the Greenians as[16]

$$G^{ss'}(\mathbf{R})=-\frac{1}{4\pi}\frac{\cos\kappa R}{R}+\sum_L i^l D_L{}^{ss'}j_l(\kappa R)\mathcal{Y}_L(\hat{\mathbf{R}})\,. \qquad (4)$$

$D_L{}^{ss'}$ are called the structure constants and are related to the $B_{LL'}{}^{ss'}$ of Eq. (1) by

$$B_{LL'}{}^{ss'}=\sum_{L''}D_{L''}{}^{ss'}C_{LL'L''}$$

and $C_{LL'L''}$ are related to the Clebsch-Gordon coefficients. We use real spherical harmonics $\mathcal{Y}_L(\hat{\mathbf{R}})$ as defined by Ham and Segall so that the structure constants are real for $E>0$. $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions. Making use of Eqs. (3) and (4), we arrive at the following expression for the structure constants.

$$D_L{}^{ss'}=P_R{}^{ss'}D_L+\kappa i^{-l}\sum_{\alpha<\sigma}{}' \exp(i\mathbf{k}\cdot\mathbf{r}_\alpha)[n_l(\kappa r_\alpha)-ij_l(\kappa r_\alpha)]\times\mathcal{Y}_L(\hat{\mathbf{r}}_\alpha)[P^{ss'}(\mathbf{r}_\alpha)-P_R{}^{ss'}]\,. \qquad (5)$$

Here, the D_L without the superscript, denotes the structure constants for a perfect lattice. The summation extends in direct space, through a neighborhood σ, and the prime on the summation indicates that $\alpha=0$ is excluded. In evaluating the second term on the right-hand side, only the real part is to be retained. Thus, Eq. (5) offers a very convenient way of calculating the structure constants for the disordered lattice. The determination of the phase shifts $\eta_l{}^{(s)}$ is straightforward. The eigenvalues are then obtained by evaluating the determinant at a sequence of energies and then locating its zero by interpolation.

III. POTENTIALS AND DETAILS OF CALCULATION

In Sec. III of Paper I, it was shown how the averaged crystal potential within a given type of the muffin-tin sphere may be determined by considering the overlap from the neighboring sites. The same procedure has been adopted here and the occupation probabilities have been calculated from the available data on the short-range order parameters. The potentials were constructed from the nonrelativistic atomic wave functions of Cu and Au obtained by Herman and Skillman[14] from the Hartree-Fock-Slater atomic calculations. The relativistic wave functions were not empolyed in view of the fact that the band calculation itself is a nonrelativistic one. The muffin-tin radii r_{mt} were chosen to be equal for Cu and Au, and r_{mt} was taken slightly smaller than the radius of the inscribed sphere for the Wigner-Seitz cell. The constant potential in the interstitial region was taken as

$$V_c=\tfrac{1}{2}[V_{\mathrm{Cu}}(r_{mt})+V_{\mathrm{Au}}(r_{mt})]\,.$$

We have computed the energies for states of different representations at the symmetry points Γ, X, and L for the disordered $\mathrm{Cu_3Au}$ at temperatures 405°, 450°, and 550°C. Cowley's short-range order parameters[3] were used for 550°C, while for the other two temperatures, results from the more accurate measurements of Moss[4] were employed. These parameters are presented in Table I.

IV. RESULTS AND DISCUSSION

In Table II, we present the results of the calculations. We choose $r_{mt}=2.46095$ a.u. In order to see how the

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[15] We refer to the equations of Paper I by using the equation numbers of that paper, but with the prefix I.

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alteration of σ affects the results, we performed calculations for $\sigma=6$ as well as $\sigma=10$. Except for $\Gamma_{25'}$ and Γ_{12} states (which changed by as much as 0.06 Ry), the change was not more than 0.004 Ry. The satisfactory convergence shows that the approximation involved in calculating the partial Greenians is not bad. Although the scheme adopted for the present calculations does take account of the short-range correlations, it is still a simplified treatment of a real disordered alloy. It was therefore felt that a very detailed calculation of the energy bands is not merited at this stage. Even with the limited calculation reported here it is possible to have an idea of the distortion of the Fermi surface, in the manner suggested by Cohen and Heine.[17] The results indicate only slight variation in the energy levels with temperature. The fact that the shifts with temperature in some of these levels are not regular is a bit unsatisfactory, and may be ascribed to the different sources of the short-range order parameters employed in the calculation.

We have not attempted a detailed comparison with the experimental data referred to in Sec. I. This is due to the fact that even for the pure noble metals, the assignment of definite transitions to the absorption peaks is still a matter of controversy.[18] If we make the common interpretation of the peaks in the optical absorptivity as due to the direct electronic transitions, we may attribute the peak at 2.4 eV observed by Nilsson and Norris[12] to the $X_5-X_{4'}$ transition. Our calculations show this to be significantly constant at 1.5 eV. We also note that when compared with the band structure of pure Cu, the positions of the *s*-*p* bands are appreciably altered, but the *d* bands (relative to Γ_1) are relatively unchanged. This explains why the soft x-ray emission for the disordered Cu_3Au is similar to that of pure Cu, and conforms to Rooke's interpretation[19] of this effect.

TABLE I. Short-range order parameters p_i for Cu_3Au employed in the present calculation.

Neighbor *i*	*lmn*	405°C	450°C	550°C
1	110	−0.218	−0.195	0.131
2	200	+0.286	+0.215	+0.105
3	211	−0.012	+0.003	+0.026
4	220	+0.122	+0.077	+0.045
5	310	−0.073	−0.052	−0.032
6	222	+0.069	+0.028	−0.009
7	321	−0.023	−0.010	−0.003
8	400	+0.067	+0.036	+0.019
9	330	−0.028	−0.015	−0.011
	411	+0.004	+0.007	+0.007
10	420	+0.047	+0.015	+0.007

TABLE II. Energy values at the symmetry points Γ, X, and L for the disordered Cu_3Au as a function of the temperature. All the energies are in Ry, and relative to the muffin-tin zero, $V_c=-1.1358$. σ denotes the order of the significant neighborhood.

	405°C $\sigma=6$	405°C $\sigma=10$	450°C $\sigma=6$	450°C $\sigma=10$	550°C $\sigma=6$	550°C $\sigma=10$
Γ_1	0.0041	0.0042	0.0041	0.0041	0.0041	0.0039
$\Gamma_{25'}$	0.5581	0.6114	0.5572	0.5994	0.6499	0.6076
Γ_{12}	0.6009	0.6410	0.5390	0.6276	0.5717	0.6469
L_{11} (lower)	0.4952	0.4933	0.4950	0.4950	0.4952	0.4828
L_{12} (higher)	0.9938	0.9906	0.9894	0.9883	1.0281	0.9790
L_2'	0.5539	0.5573	0.5544	0.5544	0.5732	0.5687
L_{31} (lower)	0.6023	0.6016	0.6022	0.6019	0.6005	0.6003
L_{32} (higher)	0.6668	0.6670	0.6673	0.6673	0.6724	0.6723
X_{11} (lower)	0.5013	0.5017	0.5004	0.5026	0.4981	0.4982
X_{12} (higher)	1.1847	1.1857	1.1861	1.1866	1.2334	1.2341
X_2	0.6548	0.6542	0.6558	0.6558	0.6604	0.6604
X_3	0.5574	0.5570	0.5565	0.5567	0.5499	0.5500
$X_{4'}$	0.7753	0.7693	0.7746	0.7714	0.7930	0.7933
X_5	0.6649	0.6684	0.6650	0.6648	0.6690	0.6690

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