Electronic Transitions in α-Phase CuGe Alloys

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(Received 13 February 1973)

The optical measurements of the α phase of CuGe alloys are interpreted on the basis of direct-transition hypothesis. The calculated energies for the interband transitions agree reasonably well with the observed values deduced from the optical measurements on the basis of some acceptable assignments.

The interpretation of optical spectra of transition and noble metals is still controversial. The interband transitions which conserve the crystal momentum $\vec{k}$ have been successfully used to interpret optical spectra of noble metals.[1] The absorptivity and reflectivity measurements of these metals and their alloys[2] lend support to the direct-transition hypothesis. The emission of optically excited photoelectrons is also interpreted in terms of the direct transitions in these metals[3,4] and their alloys.[5,6] On the other hand, Spicer and co-workers[7] try to explain photoemission spectra using the nondirect-transition (i.e., $\vec{k}$-nonconserving) hypothesis. Brust,[8] in a successful attempt to explain the photoemission and optical reflectance spectra of amorphous germanium films, finds that $\vec{k}$, although a poorly defined quantity, still has relevance. His approach is based upon a partial conservation of $\vec{k}$.

In the case of substitutional binary alloys the coherent-potential approximation (CPA)[9] is found to be the best available scheme for calculating the electronic structure of these alloys. In this method the self-energy of the electron is self-consistently determined and comes out to be complex. Spectral functions of the density of states have finite spreads. If the spectral function has a sharp peak, we can also, like Brust,[8] follow the spirit of the direct-transition hypothesis in interpreting the optical and photoemission measurements on disordered binary alloys. Recently such an approach was successfully used to interpret the optical absorption spectra of α-brass.[10] In this note we report that the same scheme works well in interpreting the optical spectra of the α-phase of Cu-Ge.

The potentials of the constituents of the alloy, i.e., copper and germanium, were calculated by employing the Mattheiss superposition prescription[11] for constructing the crystal potentials. The atomic potentials which were superposed to construct the crystal potentials were derived from the self-consistent Hartree-Fock-Slater calculations.[12] We neglected the effects of alloying such as the charge transfer and change in the lattice parameters, etc. The spectral density of states was calculated by following the method discussed in detail in an earlier paper.[13] For pure copper the spectral functions $\rho(E,\vec{k})$ are δ functions, and they acquire width on adding germanium atoms to copper. For 10-at.% germanium in copper we find the spread in $\rho(E,\vec{k})$ in the [111] direction of the Brillouin zone is about 4% of Brillouin-zone dimension. Spectral functions are sharp enough to enable us to assign an E value for a particular value of $\vec{k}$. We have calculated $\rho(E,\vec{k})$ at some selected symmetry points in the Brillouin zone in order to see whether our results could be compared with the optical data. In Table I we show our calculated values of energy (in eV) for some transitions in α-$Cu_{0.9}Ge_{0.1}$ along with the corresponding values for pure copper, which are borrowed from Smith[3] and Stocks *et al.*[14]

Rayne[15] has measured the optical absorptivity of CuGe alloys with varying concentrations of germanium up to 7 at.% at 4.2 °K. Later, Pells and Montgomery[2] measured the absorption as a function of photon energy from 1.7 to 5.9 eV for CuGe at two compositions. In both these measurements the main absorption edge at about 2.2 eV of pure copper moves to a higher energy on alloying with Ge atoms. Rayne has observed that the main peak for pure copper at about 4.2 eV shifts slightly to the

TABLE I. Some interband transitions shown for pure copper and α-$Cu_{0.9}Ge_{0.1}$. Energies are in eV.

Transitions \ Systems	Copper		CuGe	
	Theory	Expt.	Theory (10-at. Ge)	Expt.
L_{32}-L_2'	1.48[a] 1.20[d]	2.20[b,c]	2.07	2.23[b]
L_2'-L_{12}	4.67[a] 4.87[d]	4.78[c]	4.37	4.0[e]
L_{11}-L_2'	4.98[a] 4.25[d]	5.32[c]	5.41	5.4[e]
X_5-X_4'	3.99[a] 3.84[d]	3.97[c]	4.09	...

[a]N. V. Smith (Ref. 3).
[b]J. A. Rayne (Ref. 15) (for 6-at.% Ge).
[c]G. P. Pells and M. Shiga (Ref. 16).
[d]G. M. Stocks *et al.* (Ref. 14).
[e]G. P. Pells and H. Montgomery (Ref. 2) (for 8-at.% Ge).

higher energy in the alloy. Pells and Montgomery find that the single peak near 5 eV in Cu is split into two peaks in the alloy. The low-energy peak is not as pronounced as the high-energy one. The high-energy peak remains close to 5.4 eV and the low-energy one moves to the lower energies as the Ge concentration increases. Optical and photoemission measurements have been made by Nilson[6] on $Cu_{0.94}Ge_{0.06}$. His observations show the same broad features as found in the measurements of Pells and Montgomery.

In pure copper, $L_{2'}$ lies about 0.5 eV below E_F, which is depressed on alloying by an amount which depends on the total number of conduction electrons and the density of states. The Fermi energy should show a slow rise. Thus in the alloy the $(L_{2'}-E_F)$ separation will be larger than in pure copper. From our calculation we find that the $(L_{32}-L_{2'})$ separation in $Cu_{0.9}Ge_{0.1}$ is 2.067 eV. This suggests that as in the case of pure Cu, the absorption edge could be ascribed to transitions from the top of the d band to E_F. These two levels move apart as we alloy, and this agrees with the observed movement of the edge to higher energies. We adopted for the absorption peaks the interpretation of pure copper from Pells and Shiga.[16] The lower-energy peak is assumed to arise from the transitions in the neighborhood of $(L_{2'}-L_{12})$, and the higher-energy peak is associated with $(L_{11}-E_F)$ transitions. If we regard E_F to lie close to $L_{2'}$ the table shows that the calculated values show surprisingly good agreement with the experimental data. Thus we find that the optical measurements of α-CuGe can be explained on the basis of the direct-transition hypothesis.

This work was supported by the National Bureau of Standards (U. S.), Washington, D. C., under a PL 480 grant.

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