

## A study of Fermi level shifts in copper-gallium and copper-germanium alloys by x-ray absorption spectroscopy

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**Abstract.** The K x-ray absorption discontinuities of copper, gallium and germanium in pure metals as well as in six copper-gallium and three copper-germanium alloys have been studied using a Cauchois-type bent crystal spectrograph. It is observed that in all the systems the K discontinuity of copper shifts towards the higher energy side, while the discontinuities of gallium and germanium shift to the lower energy side relative to their positions in the respective pure metals. The magnitudes of the shifts are found to increase with the decrease in the content of the absorbing atom in the alloys. The observed shifts are explained on the basis of the free-electron theory of metals and the rigid-band model for alloys.

**Keywords.** Alloys; x-ray absorption spectra; Fermi level; free electron theory; rigid-band model.

### 1. Introduction

The chemical shifts in x-ray absorption spectra provide a powerful tool to study the nature of bonding in various kinds of materials (Mande 1980). Although considerable work on such chemical shifts in inorganic and intermetallic compounds has been reported in recent years (Kondawar and Mande 1976; Sarode and Chetal 1977; Ballal and Mande 1977; Ghatikar *et al* 1977; Madhusudan *et al* 1979), not much systematic work seems to have been carried out on alloys. A recent investigation carried out in our laboratory (Lokhande and Mande 1980) on gold-copper alloys shows that the chemical shifts obtained in such systems can be very well explained on the basis of the rigid-band model. We thought it worthwhile to extend our study to copper-gallium and copper-germanium alloys to obtain information regarding the electronic structure and bonding in these systems.

### 2. Experimental procedure

A Cauchois-type bent crystal x-ray spectrograph of diameter 0.4 m was used for photographing the spectra. The spectrograph was equipped with a well-tested mica crystal whose (201) reflecting planes were employed to record the spectra. A sealed Machlett x-ray tube with tungsten target, operated at 16 kV and 10 mA, was used as the source of white radiation. The wavelength measurements of the absorption discontinuities were made on microphotometer records of magnification  $\times 100$  obtained on the Spectroline Scanner manufactured by the Applied Research Laboratories,

California. The measurements were carried out using the L emission lines of tungsten as reference lines. The lines  $WL\alpha_1$  ( $\lambda = 1473.37$  X.U.),  $WL\alpha_2$  ( $\lambda = 1484.34$  X.U.) and  $WL\beta_4$  ( $\lambda = 1298.92$  X.U.) were used for the measurement of the K discontinuity of copper. The lines  $WL\beta_3$  ( $\lambda = 1260.30$  X.U.) and  $WL\gamma_1$  ( $\lambda = 1096.31$  X.U.) were used as reference lines for the measurement of the K discontinuity of gallium, while the lines  $WL\beta_3$  ( $\lambda = 1260.30$  X.U.),  $WL\gamma_5$  ( $\lambda = 1130.09$  X.U.) and  $WL\gamma_1$  ( $\lambda = 1096.31$  X.U.) were used for the measurement of the germanium discontinuity. The linear dispersion on the spectra in the region of the absorption discontinuities in the present work was found to be about 12.5 X.U./mm which agrees very well with the theoretical dispersion of the spectrograph. The dispersion on the microphotometer records was about 0.125 X.U./mm or about 1 eV/mm. A large number of measurements were made in order to obtain reliable results. It was statistically found that the error in the measurement of the positions of the discontinuities lies within  $\pm 0.5$  eV. Other details of the experimental technique can be found in the earlier publications of the laboratory (Sapre and Mande 1972; Pendharkar and Mande 1973).

The gallium and germanium metals used in this work were of A. R. grade, and copper metal of high purity was obtained from Koch-Light Laboratories Limited, Colnbrook Bucks, England. The high purity alloys were prepared by Prof. G. J. Nieuwenhuys and Dr. C. E. Snel of Kamerlingh Onnes Laboratorium der Rijksuniversiteit Te Leiden, Nieuwsteeg, Leiden, Nederland.

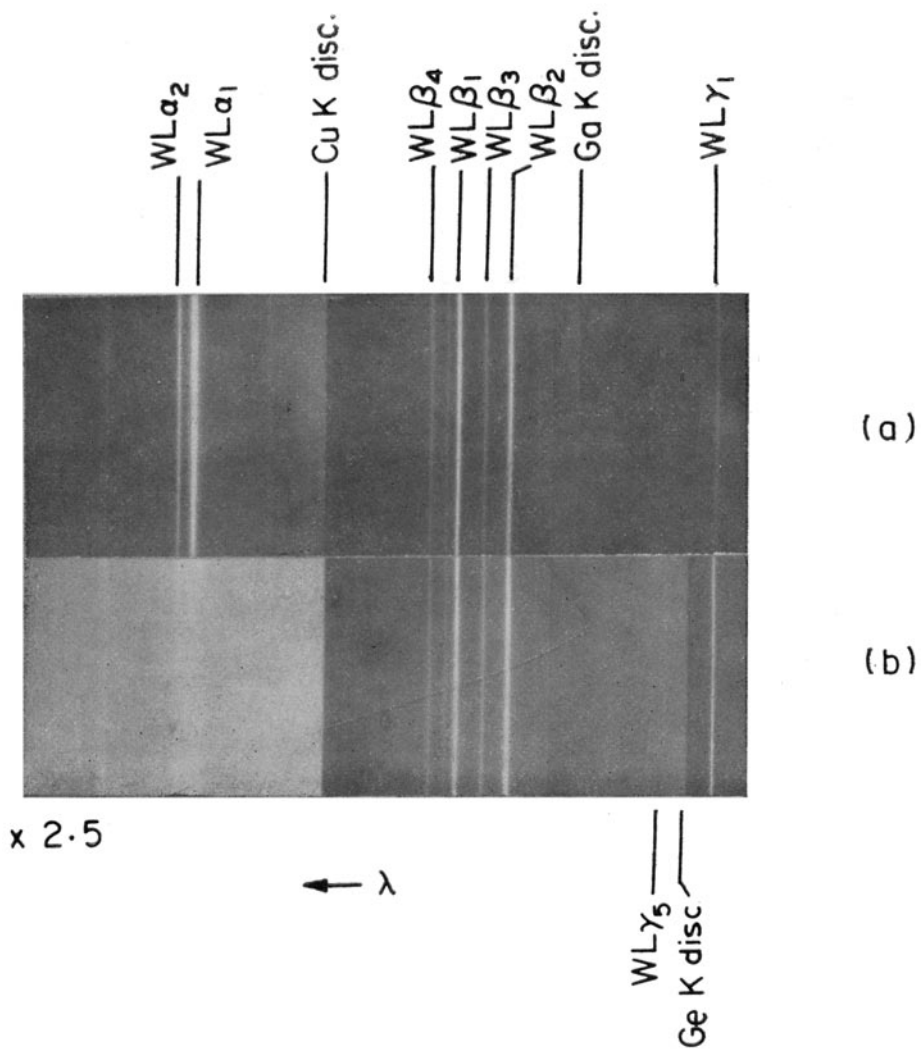
### 3. Results

A spectrogram showing the K absorption discontinuities of Cu and Ga in the  $\phi$  Cu-Ga alloy is shown in figure 1(a). Figure 1(b) shows another spectrogram depicting the Cu and Ge discontinuities in Cu-27 at. % Ge alloy.

The K absorption discontinuity of copper is found to be split into two components  $K_1$  and  $K_2$  in the pure metal as reported by earlier workers (Beeman and Friedman 1939; Mande and Joshi 1968), as well as in the alloys. No such splitting is found in the K absorption discontinuities of gallium and germanium in the pure metals or in the alloys in the present work, in conformity with the work of Sapre and Mande

Table 1. Observed chemical shifts of the K absorption discontinuity of copper in copper-gallium alloys along with theoretical shifts.

Material	At. % of copper	Wavelength $\lambda$ (X.U.)	Energy $E$ (eV)	Experimental shift $\Delta E$ (eV)	Fermi energy $E_f$ (eV)	Theoretical shift $\delta E$ (eV)
Cu metal (Ballal and Mande 1976)	100	1377.67				
Cu metal (present work)	100	1377.61	8981.10		7.00	
$\beta$ Cu-Ga	78.0	1377.38	8982.65	+1.6	8.41	+1.41
$\beta'$ Cu-Ga	76.3	1377.33	8982.97	+1.9	8.84	+1.84
$\gamma_1$ Cu-Ga	69	1377.28	8983.30	+2.2	9.17	+2.17
$\gamma_2$ Cu-Ga	65.6	1377.25	8983.50	+2.4	9.32	+2.32
$\gamma_3$ Cu-Ga	61	1377.23	8983.63	+2.5	9.29	+2.49
$\phi$ Cu-Ga	42	1377.16	8984.08	+3.0	9.76	+2.76



**Figure 1.** Spectrograms showing (a) the copper and gallium K discontinuities in  $\phi$  Cu-Ga alloy, and (b) the copper and germanium K discontinuities in Cu-27 at.% Ge alloy.

(1973) on gallium and germanium compounds. The wavelength measurements were made on the inflexion point of the discontinuities according to usual practice, on the  $K_1$  component in the copper discontinuity and on the K discontinuities in gallium and germanium. The positions of the K absorption discontinuities of copper, gallium and germanium in the pure metals as well as in Cu-Ga and Cu-Ge alloys are given in tables 1, 2 and 3. In these tables are also given the wavelengths for the copper (Ballal and Mande 1976), gallium and germanium (Cauchois and Sénémaud 1978) discontinuities reported previously for comparison. It is seen from tables 1, 2 and 3 that the K discontinuity of copper shifts towards the higher energy side and the discontinuities of gallium and germanium shift to the lower energy side in the Cu-Ga and Cu-Ge alloys with respect to the discontinuities of the pure metals. The magnitudes of the shifts are seen to increase with the decrease in the content of the absorb-

Table 2. Observed chemical shifts of the K absorption discontinuity of gallium in copper-gallium alloys along with theoretical shifts.

Material	At. % of gallium	Wavelength $\lambda$ (X. U.)	Energy $E$ (eV)	Experimental shift $\Delta E$ (eV)	Fermi energy $E_f$ (eV)	Theoretical shift $\delta E$ (eV)
Ga metal (Cauchois and Sénémaud 1978)	100	1193.65				
Ga metal (present work)	100	1193.66	10365.20		10.47	
$\phi$ Cu-Ga	58	1193.74	10364.50	-0.70	9.76	-0.71
$\gamma_3$ Cu-Ga	39	1193.77	10364.24	-1.00	9.49	-0.98
$\gamma_2$ Cu-Ga	34.4	1193.80	10363.98	-1.2	9.32	-1.15
$\gamma_1$ Cu-Ga	31	1193.82	10363.80	-1.4	9.17	-1.30
$\beta'$ Cu-Ga	23.7	1193.86	10363.46	-1.8	8.84	-1.63
$\beta$ Cu-Ga	22	1193.91	10363.02	-2.2	8.41	-2.06

Table 3. Observed chemical shifts of the K absorption discontinuities of copper and germanium in copper-germanium alloys along with theoretical shifts.

Material	At. %	Wavelength $\lambda$ (X. U.)	Energy $E$ (eV)	Experimental shift $\Delta E$ (eV)	Fermi energy $E_f$ (eV)	Theoretical/shift $\delta E$ (eV)
Copper						
Cu metal	100	1377.61	8981.10		7.00	
Cu-Ge	82	1377.33	8982.97	+1.9	9.04	+2.04
Cu-Ge	75.6	1377.21	8983.76	+2.7	9.22	+2.22
Cu-Ge	73	1377.13	8984.28	+3.2	—	—
Germanium						
Ge metal [Cauchois and Sénémaud (1978)]	100	1114.26				
Ge metal (present work)	100	1114.30	11103.79	—	11.52	—
Cu-Ge	27	1114.33	11103.10	-0.7	—	—
Cu-Ge	24.4	1114.45	11101.90	-1.9	9.22	-2.30
Cu-Ge	18	1114.48	11101.60	-2.2	9.04	-2.48

ing atoms. In figure 2 are shown curves which depict the variation of the observed shifts of the K discontinuities of copper and gallium with atomic concentration in Cu-Ga alloys. Similar curves for the Cu-Ge systems are shown in figure 3.

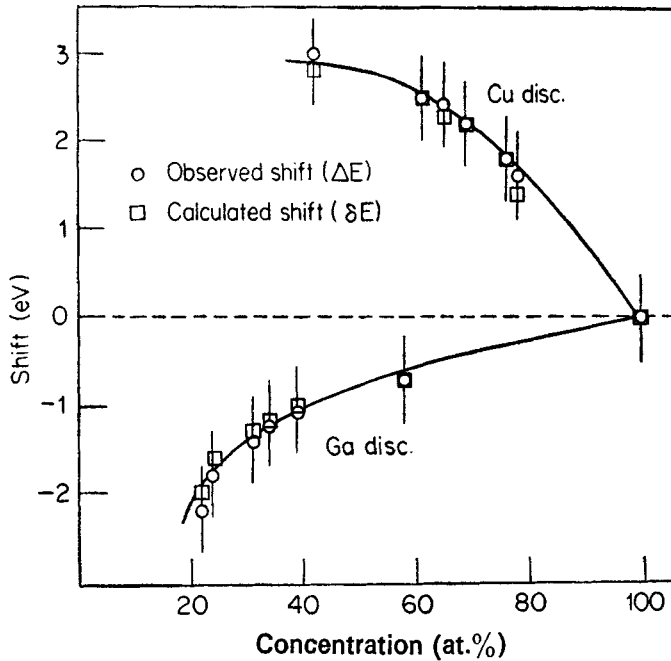


Figure 2. Variation of the observed and calculated shifts of the K discontinuities of copper and gallium with their concentrations in copper-gallium alloys.

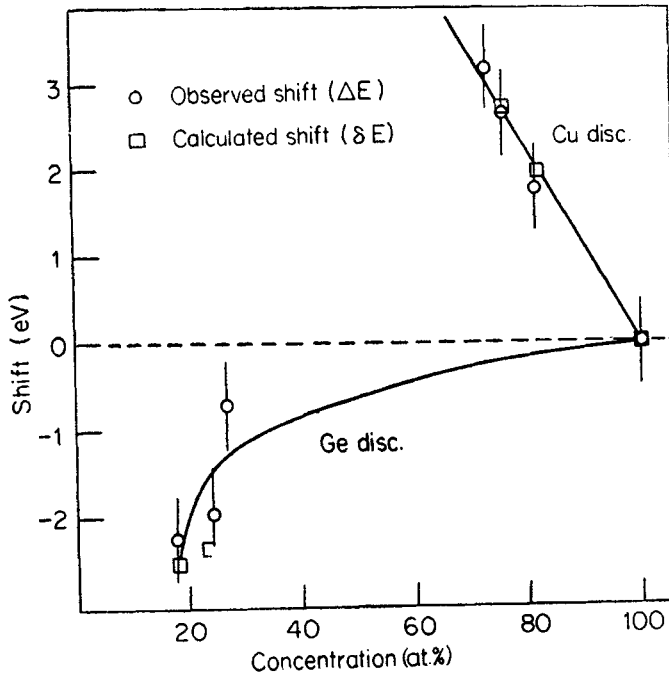


Figure 3. Variation of the observed and calculated shifts of the K discontinuities of copper and germanium with their concentrations in copper-germanium alloys.

#### 4. Discussion

It is well-known that the chemical shifts of the x-ray absorption discontinuities in compounds are governed by the nature of the chemical bonding and particularly with effective charges on the absorbing ions (Mande 1980). It has been established (Sapre and Mande 1972, 1973; Kondawar and Mande 1976; Ghatikar *et al* 1977; Madhusudan *et al* 1979; Sarode *et al* 1979) that there exists a direct correlation between the observed chemical shifts and the effective ionic charges in the case of compounds. In particular it has been shown that whenever the absorbing atom is a cation the chemical shift is towards the higher energy side and whenever the absorbing atom is an anion the shift is towards the lower energy side. Assuming our systems to be intermetallic compounds, we have tried to estimate the atomic charges on the absorbing atoms using Pauling's formula (Pauling 1960; Siegbahn 1970) which is based on electronegativity considerations. According to the electronegativity criterion in a binary compound the more electronegative element should behave as anion and the less electronegative element as cation. The electronegativity values given by Pauling (1960) are 1.9, 1.6 and 1.8 for copper, gallium and germanium respectively. Likewise, according to the electronegativity scale given by Mande *et al* (1977) the electronegativity values are 2.03, 1.77 and 2.01 for copper, gallium and germanium respectively. It is obvious from the electronegativity values on both these scales that in case the Cu-Ga and Cu-Ge systems are intermetallic compounds then copper atoms would behave as anions in them. However, our present results indicate that the chemical shifts for copper in these systems are positive, showing that there does not exist any correlation between the atomic charges and the chemical shifts for the systems studied in this work. Similarly, the negative shifts observed in the gallium and germanium discontinuities rule out the possibility of the formation of the iono-covalent bonds in these systems. It is therefore quite likely that the present systems may be considered as alloys, the bonding in which is of the metallic type just as in pure metals, and not of the iono-covalent type as in compounds. Hence we have attempted to interpret the observed chemical shifts in these systems assuming their electronic structure as in alloys on the lines of a similar study reported by us on gold-copper alloys (Lokhande and Mande 1980).

It is well-known (Richtmyer *et al* 1934; Cauchois 1948) that in the x-ray absorption process in metals the electrons from the core level are excited to empty levels in the conduction band lying just beyond the Fermi level. It has been shown (Richtmyer *et al* 1934) that because of the occurrence of a series of spectral lines which cannot be resolved one usually gets the x-ray absorption spectrum in the form of a discontinuity which resembles more or less an arc tangent curve. It is generally accepted (Sandström 1957) that the inflection point on the curve represents the Fermi limit in the case of pure metals. In more complex systems like compounds and alloys both the inner and final levels responsible for x-ray absorption may be affected, giving rise to the observed chemical shifts. However, the final levels, which participate directly in bonding, contribute to a much greater extent to the chemical shifts while the inner level being, in general, not affected appreciably does not play an effective role in producing the chemical shift. Only in the case of transition metal compounds the unfilled  $3d$  orbitals interact with the inner level and may affect the inner level to an appreciable extent. Assuming that the effect of environment on the absorbing atoms in our systems will be negligible on the core levels one can correlate the observed

chemical shifts studied in this work with the changes in the position of the Fermi level.

According to the free electron theory the general expression for the energy of the Fermi level in a metal is

$$E_f = \frac{h^2}{2m} \left( \frac{3}{4\pi} \frac{N}{gv} \right)^{2/3}, \quad (1)$$

where  $h$  is the Planck's constant,  $m$  is the free-electron mass,  $g$  is the degeneracy factor,  $N$  is the number of free electrons per unit cell and  $v$  is the volume of the unit cell. Equation (1) gives a quantitative expression for the width of the conduction band in a metal in terms of the number of valence electrons. The widths of the soft x-ray emission bands of many metals obtained experimentally are found to be in good agreement with the widths calculated by using equation (1) (Cauchois 1948; Tombouliau 1957).

Attempts have been made to describe the electronic structure of alloys on the basis of several theories (Mott and Jones 1938; Wert and Thomson 1970; Cracknell and Wong 1973). The more rigorous and sophisticated theory proposed by Friedel (1954) is valid for dilute alloys only. It has been mentioned by Biondi and Rayne (1959) that although Friedel's theory quantitatively explains the optical experimental results on dilute alloys, it does not correctly describe the screening in alloys of finite solute concentrations. Soven (1966) made approximate calculations of electronic structure of disordered alloys with special reference to alpha brass. He does not obtain complete agreement with experiments which may be because of his choice of 'far too crude' potentials.

It appears that all the rules framed by Hume-Rothery for the formation of alloys can be explained (Wert and Thomson 1970) reasonably well on the basis of the so-called 'rigid-band model'. Hummel and Andrews (1973) have shown that this model can be used to predict the behaviour of the shift of the main optical edge in the case of dilute Cu-Ga and Cu-Ge alloys. We shall make an attempt to explain our observed shifts on the basis of the rigid-band model, according to which in an alloy the electrons from the host metal and the impurity metal together form the conduction band. The band in the alloy remains practically the same as that of the host pure metal but the whole band may be shifted en block in the energy scale (Wert and Thomson 1970). In the present systems we assume that the copper atoms contribute their one  $4s$  electrons only to the conduction band, leaving the  $3d$  band unaffected—an assumption which is most likely to be true (Hummel and Andrews 1973). We also assume that in these systems the gallium and germanium atoms give three  $4p$  and four  $4p$  electrons respectively to the conduction band. Under this assumption the application of the rigid-band model may be justified in the present systems. We can now apply equation (1) of the free-electron theory to obtain the Fermi level shifts in our systems. One has simply to replace  $N$  in equation (1) by  $N'$  and  $v$  by  $v'$ , where  $N'$  now denotes the number of free electrons per unit cell and  $v'$  the volume of the unit cell in the alloy. Thus (1) is modified for alloys as

$$E_f = \frac{h^2}{2m} \left( \frac{3}{4\pi} \frac{N'}{gv'} \right)^{2/3}. \quad (2)$$

Since for the free electrons the degeneracy factor  $g$  in (2) can be taken as two and putting  $n = N'/v'$ , we have

$$E_f = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}. \quad (3)$$

Knowing the values of  $E_f$  in a pure metal and in an alloy one can calculate to a first approximation the 'theoretical shift'  $\delta E$  by writing

$$\delta E = (E_f)_{\text{alloy}} - (E_f)_{\text{metal}}. \quad (4)$$

In tables 4 and 5 we have given the relevant data (Pearson 1964) for calculating the theoretical shifts  $\delta E$  in the systems studied by us. The calculated values of  $\delta E$  may differ slightly from the values of  $\Delta E$ , the experimental shifts, depending upon the magnitude by which the band shifts as a whole in the alloys either to the lower energy or the higher energy side with respect to that of the pure metal. We have shown in

Table 4. Data for the calculation of  $E_f$  in copper-gallium alloys.

Material	Structure	Lattice parameters (Å)	Volume (V) Å <sup>3</sup>	Atoms per unit cell (Pearson 1964)	No. of electrons per unit volume ( $n$ ) $\times 10^{22}$	$E_f$ (eV)
Ga metal	Orthorhombic	$a = 4.5107$ $b = 7.6448$ $c = 4.5167$	155.75	8	15.40	10.47
$\phi$ Cu-Ga	Tetragonal	$a = b = 2.830$ $c = 5.835$	46.73	3	13.86	9.76
$\gamma_3$ Cu-Ga	b.c.c.	$a = 8.6922$	656.73	49.11	13.31	9.49
$\gamma_2$ Cu-Ga	b.c.c.	$a = 8.7315$	665.68	51.06	12.94	9.32
$\gamma_1$ Cu-Ga	Cubic (Cu <sub>3</sub> Al <sub>4</sub> type)	$a = 8.7296$	665.25	51.85	12.63	9.17
$\beta'$ Cu-Ga	b.c.c.	$a = 2.9611$	25.96	2	11.97	8.84
$\beta$ Cu-Ga	hexagonal	$a = 2.593$ $c = 4.228$	24.618	2	11.09	8.41

Table 5. Data for the calculation of  $E_f$  in copper-germanium alloys.

Material	Structure	Lattice parameters (Å)	Volume $V$ (Å <sup>3</sup> )	Atoms per unit cell (Pearson 1964)	No. of electrons per unit volume ( $n$ ) $\times 10^{22}$	$E_f$ (eV)
Ge metal	f.c.c.	$a = 5.6461$	179.988	8	17.778	11.52
Cu-18 at. % Ge	c.p. hexagonal	$a = 2.609$ $c = 4.229$	24.9289	2	12.355	9.04
Cu-24.4 at. % Ge	c.p. hexagonal	$a = 2.626$ $c = 4.559$	27.226	2	12.723	9.22
Cu-27 at. % Ge	b.c.c.	$a$ not known	—	2	—	—



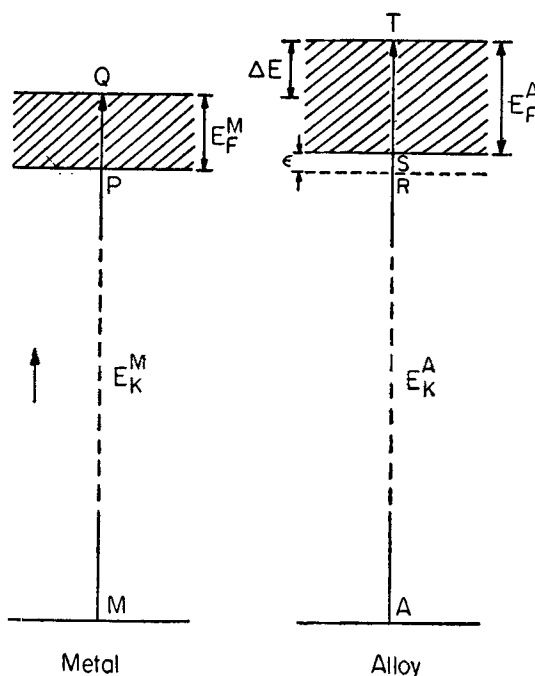


Figure 4. Energy level diagram indicating the transitions responsible for the absorption process in the pure metal and in an alloy.

figure 4, a tentative energy level diagram indicating the transitions responsible for the absorption process in the pure metal and in an alloy. It will be seen that the experimental shift

$$\begin{aligned} \Delta E &= E_k^A - E_k^M, \\ &= RT - PQ, \\ &= \epsilon + ST - PQ. \end{aligned}$$

Therefore  $\Delta E = \epsilon + \delta E$ , (5)

where  $\epsilon$  indicates the en block shift of the band. If and when  $\epsilon$  is relatively small  $\Delta E$  will be approximately equal to  $\delta E$ .

The calculated shifts obtained using (3) and (4) are included in tables 1 to 3. It is seen that the values of the experimental shift  $\Delta E$  agree fairly well within experimental errors both in sign and magnitude with the values of the theoretical shift  $\delta E$ , indicating that  $\epsilon$ , the en block shift, is negligible. In figures 2 and 3 are also indicated the points for  $\delta E$  for comparison along with the points for experimental shift  $\Delta E$ . Our work therefore shows that in alloys the chemical shifts are governed by the electronic structure and that they can be explained reasonably well with the help of the rigid-band model.

We shall now compare the results on the chemical shifts obtained by us in the copper-gallium and copper-germanium alloys. Since the valency of germanium is

four and that of gallium is three, one can expect that according to the rigid-band model the conduction band will be more rapidly filled when germanium is added to copper rather than when gallium is added to it. We can thus expect that the slope of the  $\Delta E$  vs concentration plot for the K discontinuity of copper in the Cu-Ge alloys will be larger as compared to that in the case of the Cu-Ga alloys. The  $\Delta E$  vs concentration curves for the copper discontinuity in figures 2 and 3 do show that the slope of the curve for the Cu-Ge systems is larger than that for the Cu-Ga alloys as per our expectation.

Optical absorption spectra of copper-gallium and copper-germanium alloys in very low concentration regions of gallium and germanium reported by Beaglehole and Wihl (1973) and modulated reflectivity measurements made by Hummel and Andrews (1973) have revealed that the leading edge of the copper *d* band to Fermi level transitions shifts to higher energies with increasing impurity concentration. Rayne (1961) has measured at 4.2° K the optical absorptivity of Cu-Ge alloys with germanium concentrations varying upto 7.0 at. %. Later Pells and Montgomery (1970) measured the optical absorption as a function of photon energy from 1.7 to 5.9 eV for Cu-Ge alloys of two different 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 germanium. An explanation for the higher energy shift of the edge in the  $\alpha$ -phase Cu-Ge alloys was given by Das and Joshi (1973) on the basis of the direct-transition hypothesis. Our results on Cu-Ga and Cu-Ge alloys with higher concentration of gallium and germanium show that the K absorption discontinuity of copper shifts towards the higher energy side as the impurity concentration increases. Our observations are similar to those obtained by the optical methods. Unfortunately, no optical data for Cu-Ga and Cu-Ge alloys of higher concentrations are available for direct comparison with the results obtained in our work.

## 5. Conclusions

It may be mentioned that the rigid-band model which we have used to explain the chemical shifts of our alloy systems is not applicable to transition metal alloys. In such systems the filling up of the *d* band is more important as has been shown by earlier x-ray spectroscopic studies (Farineau 1938; Mande 1960; Azároff 1966).

The chemical shifts of the x-ray absorption discontinuities obtained in compounds can very well be correlated with the effective charges on the absorbing ions and the shifts are thus characteristic of the iono-covalent bond. On the other hand, the chemical shifts in alloys of simple metals, as the present work shows, can very well be explained on the basis of Fermi level shifts and thus are characteristic of metallic bonding. X-ray absorption spectroscopy may therefore be fruitfully employed to study bond characterization in solids and thereby may help in distinguishing between intermetallic compounds and alloys of simple metals.

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