reasonable agreement with the same quantity for the solvent; fair agreement was also found in the case of Cd in Ag, where the sum for the solute was 0.004, to be compared with the experimental value of 0.006 for the silver and a computed[2] (square-well) value of 0.003.

The linewidths of Al, Sn, and P in Cu were all 4.5 to 5.5 G and very slowly dependent upon solute concentration. The dipolar contribution accounted for the major part of the width and the inhomogeneous Knight shift was probably responsible for the balance. Because of the errors involved in the measurement of total linewidth and the large proportion of dipolar width an analysis of the type carried out for the Sn and Cd in Ag alloys was not feasible.

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X-Ray *K* Absorption Spectra of Cu-Ni Alloys*

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Copper and nickel *K* absorption spectra have been measured in the pure metals and in four alloys, respectively, containing 17.2, 26.0, 43.3, and 65.6 at.% copper. Variations in the absorption-edge fine structure of both metals were observed in the nickel-rich solid solutions. These variations are interpreted by considering the electronic configurations of the individual absorbing atoms and how they are altered by alloying. It is proposed that the *K* absorption spectrum of each constituent should be different and should not reflect a common density-of-states distribution for the alloy. It is also shown that this model can be applied to explain the x-ray emission spectra observed by others.

I. INTRODUCTION

THE difficulties associated with the selection of a suitable model for interpreting x-ray emission and absorption spectra in solids have been described previously.[1–3] In x-ray emission, the filling of an inner electron vacancy in an atom by one of the outer electrons is accompanied by the emission of an x-ray quantum having the corresponding energy. Conversely, in x-ray absorption, an incident x-ray quantum is absorbed provided its energy is sufficient to excite an inner electron to one of the normally unoccupied outer states. Thus, emission spectra of solids are related to the availability and energy distribution of valence-conduction electrons whereas their absorption spectra are related to the normally empty higher energy state distributions. The actual transitions are determined by quantum-mechanical transition probabilities which are usually too complicated to evaluate quantitatively except for determining the symmetries of the initial and final states (selection rules). The interpretation is further complicated by the fact that the excited atom may act as a perturbation, that is, it superimposes its own localized discrete states onto the energy bands of the solid. Despite these difficulties, which have prevented the development of a rigorous quantitative theory, repeated efforts have been made to deduce the general features of energy bands in solids, such as their shapes, widths, and degree of occupation.

The present investigation was undertaken primarily to determine what correlations, if any, could be established between the fine structure observed in x-ray absorption spectra of alloys and their electronic structure. To date, essentially three kinds of correlations have been proposed. In 1939, Beeman and Friedman[4] demonstrated quite clearly that the absorption-edge structure of copper and nickel could be explained by the then recently calculated energy-band model of these metals.[5,6] The validity of this correlation has been re-emphasized by Burdick[7] who found that it agreed with his recalculation of the energy-band structure of copper. Nemnonov[8] has extended this approach by attempting to correlate the presumed electronic structures of transition metals, their alloys, and their compounds, to displacements (along the energy scale) of certain portions of the absorption edge. As pointed out below, the exact location of inflections or other characteristics of the absorption-edge curves along the energy scale is subject to considerable error so that the efficacy of this procedure is uncertain. Similarly, specific correlations of the fine structure to plasma oscillations

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in the absorbing solid[9] have yet to be proven. It is doubtful that such interactions affect the fine structure within 20 eV of the main edge[2] and, as pointed out by Singh[10] for the case of iron, the extended structure can be explained equally well by existing theories (cf. Ref. 3).

In view of their successful explanation of the K absorption spectra of Cu and Ni, Friedman and Beeman[11] examined several solid solutions formed by these same metals. Possibly because they expected to find a common fine structure for both metals in the alloy, they reported no significant changes on alloying and attributed this to a lack of correspondence between the band model for the elements and that of the alloys. In a companion paper, however, Bearden and Beeman[12] did report observed changes in the fine structure of the zinc K edge in Ni-Zn alloys. Somewhat earlier, Hayasi[13] had examined a 50:50 Cu-Ni alloy and also failed to observe significant changes in the K absorption-edge structures of the metals in this alloy. It will be shown below that, using a very careful experimental procedure, systematic changes in the fine structure of the absorption edges of both metals upon alloying do become manifest and can be interpreted by focusing attention on the electronic structure of the absorbing atom within the alloy rather than that of the solid as a whole.

II. METHOD OF MEASUREMENT

The starting materials were 99.95+ conductor grade copper and 99.95+ electrolytic nickel. Four Cu-Ni alloys spanning most of the solid-solution range were prepared by vacuum melting and the ingots were slowly cooled to insure thorough homogenization. The pure metals and the alloys were reduced to foils approximately ten microns thick by successive rolling and vacuum annealing. The samples were examined metallographically and by x-ray diffraction and, as far as could be determined, formed random solid solutions, as expected.

The foils were mounted in a two-crystal spectrometer equipped with two silicon crystals, each having half-widths of approximately 7 sec for the range of x-ray wavelengths used. This permitted significant measurements to be made in ten-second intervals. The absorption coefficient at each point was determined in the usual way by measuring the ratio of the x-ray intensity transmitted through the foil to that incident on it. Although the stability of the x-ray source used was within 1/10 of 1%, the direct beam intensity was checked before and after each measurement, whose over-all statistical accuracy is estimated to lie within ±1%. Finally, the absorption coefficients determined in this way as a function of energy were corrected for instrumental affects by determining the spectrometer "window" as suggested by Parratt and Hempstead[14] and using an IBM-1620 program based on one first prepared by Porteus.[15]

The linear absorption coefficient μ of a binary alloy can be expressed as follows:

$$\mu=\rho(p_A\mu_{mA}+p_B\mu_{mB})\,, \tag{1}$$

where p_A and p_B are the weight percent and μ_{mA} and μ_{mB} the mass absorption coefficients, respectively, of the two elements A and B comprising the alloy, while ρ is the density of the alloy. Since it is desired to observe the variation of only one of the two absorption coefficients as a function of x-ray energy, it is necessary to predetermine the values of the mass absorption coefficient of the other component in the same energy range. This was done using the foils of the two pure metals, and, as expected, μ of each element was found to be a very slowly varying function of energy near the other metal's absorption edge. Knowing the absorption coefficient of one element, it is possible to rearrange the terms in Eq. (1) to solve for the linear absorption coefficient of the other element, say, μ_A directly in terms of the measured μ values of the alloy.

$$\mu_A=\rho_A\mu_{mA}=\frac{\rho_A}{p_A}\left(\frac{\mu}{\rho}-p_B\mu_{mB}\right). \tag{2}$$

The advantage in normalizing the experimental data in this way is that one obtains values for the absorption coefficients that are independent of composition and therefore are directly comparable with each other. It should be noted that in practice, however, the absolute determination of μ is complicated by uncertainties in the foil thickness and porosity. Thus it is really safe only to compare the relative heights of comparable portions of absorption curves obtained from individual foils. The energies corresponding to the inflections, extrema, or other characteristics of the absorption curves are subject to maximum experimental errors so that relative changes from foil to foil can be trusted only when they are quite large. In the present study, it was felt that the observed energy changes were too small to be deemed reliable.

III. INTERPRETATION OF EXPERIMENTAL RESULTS

The linear absorption curves for nickel and for copper for three of the four alloys studied, are shown, respectively, in Figs. 1 and 2. The fourth alloy, containing 65.6% Cu, yielded absorption curves identical to those of the 43.3% alloy. In each case, the dashed curves represent the alloy indicated and are superimposed on a solid curve representing the absorption in the pure

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metal, to facilitate comparisons. Before proceeding with the interpretation of the alloy curves, it is worthwhile to review briefly the arguments put forth by Beeman and Friedman[4] to explain the absorption curves of the two pure elements. The first maximum in the *K* edge of nickel (solid curves in Fig. 1) must be due to transitions to empty states lying just above the Fermi energy (marked $E=0$ in the figure) in the metal. Beeman and Friedman assumed that these are dipole transitions to the unfilled $3d$ states in nickel since these states have admixed p-state symmetry in the metal. Beyond this initial rise, absorption increases continuously as the p character of the empty states increases, reaching a maximum at about 15 eV above the Fermi energy, corresponding to the density-of-states maximum of the empty $4p$ states. The transition probabilities are assumed to be primarily a function of the selection rules in this energy region. The interpretation advanced for the absorption curve of copper (solid curves in Fig. 2) is quite similar. Above the Fermi energy in copper, the rise in absorption is due to transitions to empty $4s$ states which have admixed $4p$ symmetry. As pointed out by Burdick,[7] at about 4 eV above the Fermi energy the empty states have mostly s-like symmetry (absence of p symmetry) so that the dipole transition probability declines and there is a minimum in the absorption curve. With increasing energy it again rises to a peak corresponding to the $4p$ density-of-states maximum in copper.

In view of the similarity of the electronic configurations and crystal structures of copper and nickel, it is reasonable to expect that the energy-band model of Cu-Ni solid solutions should resemble that of either constituent. This is the basis of the collective-electron model first advanced by Mott[16] in which it is assumed that, if the fraction x of Cu is added to the fraction $1-x$ of Ni, the number of holes remaining in the $3d$ band is $0.6-x$ so that the $3d$ band becomes completely filled when 60% Cu is present. The general correctness of this model has been amply demonstrated by observations of the systematic decline in the $3d$ hole density in magnetic susceptibility and electronic specific-heat measurements. As shown in the next section, this model has been used previously to interpret x-ray spectra of Cu-Ni alloys on the assumption that the spectra of both constituents should be alike, in a given alloy, since they should be characteristic of the density-of-states distribution for the alloy. As can be seen in Figs. 1 and 2, the spectra of Cu and Ni in the alloys resemble more closely those of the pure metals than they do each other. Similar observations have led previous investigators to the conclusion that, possibly, a common density-of-states curve or band model does not exist for the alloys.

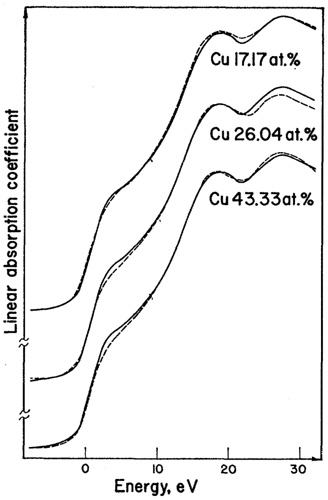

FIG. 1. Fine structure of Ni *K* absorption edge in pure nickel (solid curves) and Cu-Ni solid solutions (dashed curves). In superimposing each pair of curves, the first inflection in each curve was set at $E=0$ (Fermi level).

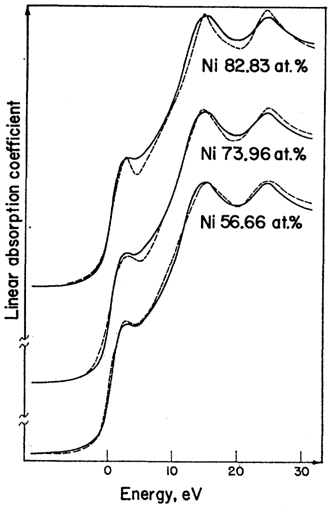

FIG. 2. Fine structure of Cu *K* absorption edge in pure copper (solid curves) and Cu-Ni solid solutions (dashed curves). In superimposing each pair of curves, the first inflection in each curve was set at $E=0$ (Fermi level).

A reconsideration of the x-ray absorption process suggests a possible alternative explanation. Beginning with pure nickel, the outer electron distribution of an "average" atom gives the configuration $3d^{9.4}4s^{0.6}$. The absorption of an x-ray quantum, however, takes place in an atom whose actual electronic configuration is either $3d^9 4s^1$ (60% probability) or $3d^{10}4s^0$ (40% probability). Thus, the *K* absorption spectrum of pure nickel (solid curves in Fig. 1) is a superposition of the absorption spectra of the two kinds of nickel atoms. The valence-conduction states are exactly those calculated, for example, by Burdick[7] except that the excited atom momentarily lacks an inner electron so that the energies of its valence-conduction states may be slightly altered in such ways as has been proposed, for example, by Parratt.[2]

In the energy range being considered, the $1s$ electron ejected in the absorption process does not gain sufficient energy to leave the immediate vicinity of the parent atom. Thus it can undergo transitions only to one of the empty valence-conduction states of the parent atom or one of the hybrid states formed with its nearest-

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[16] N. F. Mott and H. Jones, *The Theory and Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936; reprinted by Dover Publications, New York, 1958), p. 196.

neighbor atoms via overlapping orbitals. Consequently, the substitution of copper atoms for nickel atoms in the solid solution can have one of two consequences: When copper atom ($3d^{10}4s^1$) replaces the first kind of Ni (60% probability) then it simply removes one $3d$ hole. When a copper atom substitutes for the other kind of nickel atom (40% probability) then the $4s$ electron is demoted to an empty $3d$ state so that it doesn't raise the Fermi energy of the alloy. This model obviously leads to the same predictions of magnetic susceptibility and specific heat that the collective-electron model of Mott does and is of value primarily when phenomena taking place in the immediate vicinity of individual atoms are being considered.

Using this viewpoint, it immediately becomes clear why the absorption edges of copper and nickel should retain their fine structure in the alloy. In fact, the changes in the fine structure now can be correlated directly to changes in the electronic structure of the absorbing atoms and, from this, to the nature of the interatomic interactions. Thus, the progressive decline in the first maximum of the nickel edge simply reflects the diminution in the density of $3d^9$ nickel atoms as the fraction of copper atoms increases. The failure of this maximum to disappear entirely even in a 65% Cu alloy suggests that there are either some $3d^9$ configurations remaining or that there are allowed transitions to states having possible $4(s-p)$ symmetry lying at the same energy level. Similarly, the progressive increase in the first maximum in the copper K edge, as more nickel is added to copper, Fig. 2, results from the increasing number of atoms having $3d^{10}4s^0$ configurations. (These may be copper atoms that "donated" their $4s$ electrons or nearest-neighbor $3d^{10}$ nickel atoms.) The pronounced sharpening of the maxima of the uppermost curve in Fig. 2 (83% Ni alloy), reflecting a possible sharpening of the copper valence-conduction states, probably is caused by the wider dispersion of copper atoms in this alloy.

According to a recent calculation by Irkhin,[17] the relative probabilities of dipole to quadrupole transitions in the K absorption process in Cu and Ni are in the ratio of 100:1. It follows, therefore, that the above model can be used to interpret successfully the absorption spectra of the pure metals and the Cu-Ni alloys. In other words, the fine structure of the K absorption edge does not reflect the density-of-states curve of the alloy but the electronic structure (outer orbitals) of the absorbing atom. It is shown in the next section that this model is equally successful in explaining the x-ray emission spectra of these alloys.

IV. DISCUSSION

It is of obvious interest to compare our observations to those of others. Although Friedman and Beeman failed to observe any changes in the Cu or Ni K absorption edges with alloying, they did observe small changes in their $K\beta$ emission lines which they attributed to a decrease in $3d$ band dipole radiation with increasing nickel.[11] Similarly, Farineau and Morand[18] observed little dependence of the L spectra of Cu and Ni on composition in several Cu-Ni alloys, except for a slight narrowing of the emission lines when the emitting atoms were present in small concentrations. Finally, the very careful measurements of Clift, Curry, and Thompson[19] of the Cu and Ni M emission spectra retain the forms characteristic of the pure metals throughout the entire range of alloy compositions. In fact, the relative intensities of the lines vary in direct proportion to the ratio of the atoms in each alloy examined. This is, of course, exactly what one should expect in these alloys. Since the emission process is predominantly an atomic process, the location of the atom inside a particular alloy merely determines the relative energies, symmetries and spatial distributions of its valence-conduction electrons. Thus, the direct proportionality of the emission-line intensities to the atomic ratio simply reflects the relative change in kinds of atoms available for excitation. The fact that Clift *et al.* did not observe any significant changes in the line shapes on alloying or the existence of a "common" emission band for the alloy does not justify their conclusions, however, that "these results appear not to be consistent with the assumption of a common valence band, with complete sharing of electrons."[19] The observed K, L, and M emission spectra simply show that they are insensitive to the structure of such a common valence band and to the electron sharing that definitely appears to take place in nickel-rich Cu-Ni alloys. This last point deserves additional comment. The nickel emission line observed by Clift *et al.* shows an always-present tail on the high-energy side which is probably a reflection of the $4s$ electron transitions (cf. Ref. 16, p. 127) while the main line reflects the average number of $3d$ electrons per atom. In Cu-Ni alloys, this average number presumably changes from 9.4 in pure nickel to 10.0 in the 60% Cu alloy, or a maximum change of 6% which is probably too small to be detectable by the experimental procedures available for the study of emission spectra. Conversely, the average number of $4s$ electrons per copper atom changes by as much as 40% on alloying so that some variations should manifest themselves in the emission spectra. An examination of the emission curves of Clift *et al.*, for alloys containing 30% Cu or less (their Fig. 7), shows a suggestion of variations on the high-energy side of the copper line. Unfortunately, this portion overlaps the relatively pronounced high-energy tail of the nickel line so that these variations are partly obscured.

Another observation meriting brief discussion is the failure of the curves shown in Figs. 1 and 2 to display continuous dependence on composition for alloys con-

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taining more than 45% Cu. One possible explanation of this could be a change in the unknown transition probabilities which render such transitions less likely in copper-rich alloys. A more likely one is that the relative transfer of copper 4*s* electrons tends to decrease as the number of copper atoms increases. The retention of some 3*d* holes, even beyond the 60% Cu composition predicted by Mott, is supported by recent observations of the magnetic susceptibility of Cu-Ni alloys[20–22] and their electronic specific heats.[23,24] A particularly intriguing suggestion, in view of the x-ray absorption spectra described above, is that due to an incipient miscibility gap in the copper-nickel system, there is a tendency toward segregation of nickel atoms in copper-rich alloys.[25] Since such clustering would minimize electron sharing between segregated copper and nickel atoms, it would serve to retain a number of $3d^9$ configurations in the alloy, thus explaining the x-ray absorption edges and the magnetic- and specific-heat measurements.

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Some Properties of a Double Acceptor Center in CdTe*

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When CdTe and other II-VI semiconducting compounds are heat treated with an excess of the cation component or are subjected to high-energy electron bombardment, a double acceptor is produced that has its second charged state close to the conduction band. The defect is characterized by its unique properties manifested in electrical transport and photoconductivity measurements. This paper deals with this imperfection in CdTe. It is shown that all of the observed properties associated with the defect are consistent with the double acceptor model. The energy of the doubly ionized state is 0.06 eV below the conduction-band minimum. In this state the defect is an effective hole trap at low temperatures. Electrons are strongly inhibited from recombining at the singly ionized center by an effective "barrier" of 0.27 eV. At moderately low temperatures ($T \lesssim 85$°K), this phenomenon leads to marked departures from electronic equilibrium. On the basis of the preparative conditions leading to the center's production, it is suggested that the imperfection involves a native defect, most probably a vacancy, associated with a chemical impurity. Another defect with a level 0.6 eV below the conduction band, reported earlier by deNobel in heavily doped material, is found to be produced in samples fired under moderately low cadmium pressure. From the firing conditions and the Hall data it is inferred that this level is also due to an intrinsic imperfection.

INTRODUCTION

THE effects of departures from the ideal stoichiometric ratio on the electrical and optical properties of some compound semiconductors are well known. When these deviations are large relative to residual impurity concentrations, such as in the chalcogenides of lead[1] and tin,[2] certain induced properties can readily be ascribed to the created native defects. Most compound semiconductors, however, have rather small shifts from the stoichiometric ratio. The magnitude of the deviation is often less than the residual impurity concentration so that the properties of native defects are obscured. In a broad survey of the properties of CdTe, deNobel[3] studied the electrical behavior of *n*-type material as a function of impurity and stoichiometry. From his studies, he concluded that interstitial Cd atoms give rise to single-donor levels 0.02 eV below the conduction band. The concentration of this imperfection increased in direct proportion to the Cd pressure and could be sufficiently large under high P_{Cd} to dominate the electrical properties. However, in similar studies, Yamada[4] was unsuccessful in attempts to obtain *n*-type CdTe by means of stoichiometric deviations.

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