Clustering Effects and the Rigid-Band Model in Cu-Ni Alloys*

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(Received 6 June 1969; revised manuscript received 18 July 1969)

The effects of clustering on optical and photoemission data for Cu-rich Cu-Ni alloys are examined. Clustering cannot explain the experimental observations, which are consistent with a virtual-bound-state model rather than a rigid-band model.

IN a recent Letter,[1] Kidron has concluded from his small-angle x-ray diffraction data and other data for Cu-Ni alloys that important clustering effects occur in this alloy system. Because of these effects, Kidron[1] has questioned the interpretation by the present authors[2] and others[3] that optical and photoemission data for Cu-rich Cu-Ni alloys are consistent with a virtual-bound-state[4] model rather than with the rigid-band model.[5] We examine in this paper the effects that extreme clustering would have on the previously reported photoemission data and establish that the assumption of extreme clustering could not account for the experimental observations.

The existence of a miscibility gap for the Cu-Ni alloy system for low temperatures and intermediate compositions, with attendant short-range ordering and clustering, is now well established.[6] From his analysis, Kidron[1] has concluded that in a 50%-Cu–50%-Ni alloy clusters containing 70% Ni atoms and 44 atoms in each exist and constitute 18–55% of the volume of the alloy specimen. The remaining volume was found to be of the average (50-50) composition. The extent of clustering effects in any alloy specimen is strongly dependent upon the thermal history of that specimen, and the clustering found by Kidron may indeed apply to his particular sample, which was heated 50 h at 300°C.

In order to minimize the possibility of clustering, the alloy specimens used in photoemission measurements were, as mentioned in Ref. 2, homogenized by annealing at high temperatures and quenching. Specifically, the 87%-Cu sample (identified as 90% Cu in Ref. 2) was heated at 1000°C for 14 days and the 77%-Cu sample was heated at 960°C for 13 days. Both samples were air-quenched. Before photoemission and reflectivity measurements, the specimens were heated to about 500°C for a total of about 12 h to clean the surfaces. By using argon-bombardment cleaning on one sample of composition 77% Cu, the total heating time at 500°C was reduced to about 2 h with no appreciable change in the photoemission results.

The recent work of Hicks, Rainford, Kouvel, Low, and Comly[7] and of Robbins, Claus, and Beck[8] indicates clearly that a local moment develops when a small region of a Cu-Ni alloy becomes sufficiently Ni-rich. However, it seems clear from the results of Ryan, Pugh, and Smoluchowski[9] and of Pugh and Ryan[10] that such moments do not appear in properly homogenized alloys containing less than about 30% Ni. As detailed above, our samples were homogenized. The only question remaining is whether the subsequent heat-cleaning treatments at 500°C caused important clustering effects. As will be outlined below, we can find no evidence that this is the case.

Kidron's analysis relies heavily on the magnetic susceptibility data of Ryan, Pugh, and Smoluchowski[9]; therefore, it is important to note that on the basis of these data, Pugh and Ryan[10] question the validity of the rigid-band model for Cu-rich Cu-Ni alloys. Klein and Heeger[11] have shown that the virtual-bound-state model, which is used to interpret the photoemission data,[2] can also explain the susceptibilities that are observed for Cu-Ni alloys.

In the interpretation of photoemission data for Cu-rich Cu-Ni alloys,[2] the conclusion that the rigid-band model does not hold rests upon two observations. First of all, the Cu d state to Fermi-level (E_F) energy separation remains constant (to within ± 0.1 eV) upon alloying up to 23% Ni with Cu. Also, there is a large increase in the number of states in the free-electron-like bands of Cu (between E_F and 2 eV below E_F) as Ni is added to Cu (Figs. 1 and 2 of Ref. 2).

Considering the first indication, suppose we *assume* that the rigid-band model does hold for Cu-rich alloys and we make the rather extreme assumption that in the alloy containing 23% Ni, 25% of the volume is made up of clusters containing 70% Ni. Then the remaining 75% of the volume would contain 7.6% Ni. The contribution from the Cu-rich portion of the volume would dominate the energy distribution curves (EDC's) and from the rigid-band model the Cu d state to Fermi-level energy separation would be[5] $7.1[(1-x)^{2/3}-0.6^{2/3}]\text{eV}=1.7$ eV instead of the observed 2.0 eV. In

* Work supported by the National Science Foundation and by the Advanced Research Projects Agency through the Center for Materials Research at Stanford University.

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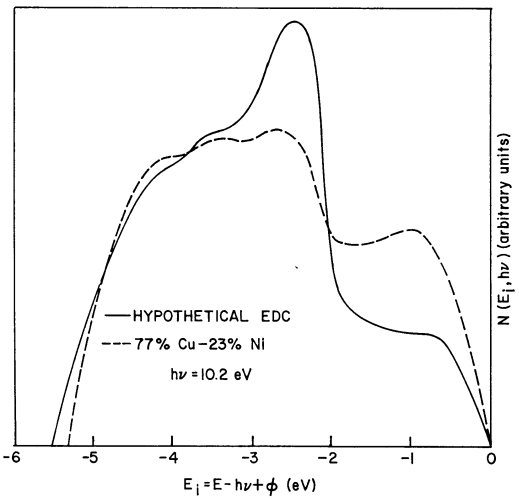

FIG. 1. Hypothetical EDC made by superimposing 0.77 times a pure-Cu EDC and 0.23 times a pure-Ni EDC compared to the curve measured for a 77%-Cu–23%-Ni alloy.

other words, unless almost all of the Ni were contained in Ni-rich clusters (which is not suggested by any interpretation), there should still be a discernible shift in the Cu d state to E_F energy separation if the rigid-band model held.

EDC's for pure Ni [12] have a sharp peak just below E_F. Therefore, it might be thought that the observation of a peak at 1 eV below E_F in Cu-rich Cu-Ni alloys could result if the Ni in these alloys was contained in clusters and the alloy EDC's were therefore a superposition of results from almost pure Cu and almost pure Ni regions. This possibility can easily be rejected, however. Suppose we make the extreme assumption that in a 77%-Cu–23%-Ni alloy all of the Ni atoms are in clusters of almost pure Ni. If these clusters contained about 50 atoms and had a spontaneous magnetic moment, they would also have an electronic structure characteristic of almost pure Ni. The photoemission results would then be a superposition of photoemission from the Ni-rich clusters and the remaining Cu-rich material. Since the quantum yields and the optical absorption strengths of pure Ni and pure Cu are nearly identical for the energies of interest, greatly different optical matrix elements would not be expected for the two different regions. In Fig. 1, a hypothetical EDC corresponding to the above situation has been made by superimposing 0.77 times a pure Cu EDC and 0.23 times a pure Ni EDC at $h\nu = 10.2$ eV. The EDC's for pure Ni and pure Cu were obtained in the course of the alloy photoemission studies on samples with surface preparation similar to that used for the alloys.[2] The EDC actually measured for 77%-Cu–23%-Ni is also shown in Fig. 1. The vertical scale of the figure is arbitrary, although the heights of the two curves were adjusted to match approximately the heights of the Cu d-state structure below −2 eV. The hypothetical EDC is clearly quite different from the actual EDC: The first peak in the hypothetical EDC occurs at −0.6 instead of −1.0 eV (and, in fact, is not very pronounced) and the peak height is less than 40% of the Cu d-state structure. In the actual curve the −1.0-eV peak has about 60% of the height of the Cu d-state structure. By assuming Ni-rich clusters with an electronic structure characteristic of Ni, the nine d electrons per Ni atom have been spread over an energy range of 5–6 eV. Consequently, the magnitude of the Ni density of states in any energy range is reduced, and the observed strength of structure at −1.0 eV cannot be obtained. On the other hand, the virtual-bound-state model used in Ref. 2 constrains the nine Ni d electrons to be contained in an energy range of 1–2 eV. This causes a large density of electrons per eV and accounts for the strong strength that is observed for the −1.0-eV peak in the alloy. In other words, strong structure in the Cu-rich alloys at −1.0 eV is consistent with the localization in energy of the Ni d electrons as predicted by the virtual-bound-state model; it is not consistent with assuming that distinct clusters of almost pure Ni exist in the alloys.

One final comment concerning the relationship of the results from Cu-Ni alloys to results from other alloy systems can be made. Many noble-metal–transition-metal alloy systems, including Au-Ni,[13] Au-Pd,[14] Cu-Pd,[15] Ag-Pd,[16] Cu-Mn,[17] and Ag-Mn,[15] have recently been studied using optical and/or photoemission measurements. These measurements have shown that a virtual-bound-state model rather than the rigid-band model is appropriate for understanding alloy properties. Clustering effects would be expected to vary greatly in these different alloy systems, but the alloying behavior of all is consistent with the virtual-bound-state model. The interpretation of the properties of Cu-Ni alloys in terms of the virtual-bound-state model is consistent with the systematics of these other alloy systems; therefore, it seems highly unlikely that in this particular alloy system the experimental observations could be caused by clustering.

Thus we feel that strong clustering effects reported for Cu-Ni alloys near 50-50 composition are not present in alloys of more dilute Ni content. In such dilute alloys, the assumption of extreme clustering and a rigid-band model cannot explain the observed photoemission and optical data. A virtual-bound-state model does give a much more adequate basis for understanding the observations.

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