obtain the following result:

$$\sigma_{xx}=\frac{nec}{H_0}\frac{(m_c^2/m_1)cv}{eH_0}\times\left\{1+\frac{3}{4}\frac{m_3}{m_2}\frac{\cos^2\phi\cos^2\theta}{\cos^2\psi}\left(\tan\theta-\frac{m_2}{m_3}\tan\phi\right)^2\times\left[\frac{1}{r}(1+r^2)^2\tan^{-1}\left(\frac{1}{r}\right)-r^2-\frac{5}{3}\right]\right\},\qquad\text{(A9a)}$$

$$\sigma_{yy}=(nec/H_0)m_1cv/eH_0,\qquad\text{(A9b)}$$

$$\sigma_{zz}=3\frac{nec}{H_0}\frac{eH_0}{(m_1m_2m_3/m_c^2)cv}r^2\left[1-r\tan^{-1}\left(\frac{1}{r}\right)\right],\qquad\text{(A9c)}$$

$$\sigma_{yx}=nec/H_0,\qquad\text{(A9d)}$$

$$\sigma_{zx}=-\frac{nec}{H_0}\times\left\{\tan\psi+\frac{3}{2}\frac{m_c^2}{m_1m_2}\frac{\cos\phi\cos\theta}{\cos\psi}\left(\tan\theta-\frac{m_2}{m_3}\tan\phi\right)\times\left[r^2-r(1+r^2)\tan^{-1}\left(\frac{1}{r}\right)\right]\right\},\qquad\text{(A9e)}$$

$$\sigma_{zy}=0,\qquad\text{(A9f)}$$

$$1/r=p_{zm}/|b|=q_zl,\qquad\text{(A10)}$$

where l is given by Eqs. (55) and (A7).

PHYSICAL REVIEW B VOLUME 1, NUMBER 4 15 FEBRUARY 1970

Low-Temperature Specific-Heat Study of Cu-Pd Alloys

Y. Sato, J. M. Sivertsen, and L. E. Toth
Department of Metallurgy—Material Science, University of Minnesota, Minneapolis 55455

(Received 4 September, 1969)

Variations with composition of the electronic specific-heat coefficient γ and Debye temperature Θ_D have been determined for Cu-Pd alloys from low-temperature specific-heat measurements between 1.5 and 4.2°K. The dependence of γ on composition is similar to that found by Hoare *et al.* for Ag-Pd alloys. For Cu alloys with small concentrations of Pd, deviations from a rigid-band model have been observed. Thermodynamic properties of these alloys are discussed in terms of the band structure deduced from γ values. Changes in long-range order and short-range order have pronounced effects on γ and Θ_D values.

I. INTRODUCTION

The phase diagram for Cu-Pd shows that there exists a continuous solid solution (fcc) above 600°C, and that below 600°C there are three superlattice structures: α' (ordered fcc), α'' (ordered fct), and β (ordered bcc).[1] In Pd-rich alloys, x-ray diffuse scattering results by Chen[2] indicate local clustering. In this paper we have studied the effects of long-range order in the β phase and local clustering in Pd-rich alloys on the low-temperature specific heats in relation to the energy band structure and the thermodynamic properties. We have also investigated the effect of dilute concentrations of Pd on the electronic specific heat in the Cu-rich alloys.

The effect of superlattice formation (long-range order) on the electronic structure has been considered by several authors.[3–5] Nicholas[5] has suggested that when an alloy develops a superlattice the interaction between the Fermi surface and new Brillouin zone boundaries, corresponding to the extra Bragg reflections, splits the energy band. The density of states at the Fermi surface may change depending upon the position of the Fermi level in the energy band. Furthermore, changes may occur in the lattice contribution to the specific heat.[6]

Chen[2] has observed that the local order coefficients α_1 of Pd-rich alloys are positive indicating clustering and that the degree of clustering increases with temperature. These results were partially substantiated by Myles and Darby[7] using vapor-pressure measurements. These results are somewhat puzzling in view of the phase relationships found in this system. Since the β phase has a superlattice structure (CsCl-type structure) we expect short-range order rather than clustering to prevail at compositions close to the β phase. Furthermore, large negative values of the heat of mixing[8] also suggest that pairs of unlike atoms are formed if a simple

---

[1] P. M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Co., New York, 1958).

[2] T. Chen, Ph.D. Thesis, University of Minnesota (unpublished).

[3] T. Muto, Sci. Paper. Inst. Phys. Chem. Research (Tokyo) **34**, 377 (1938).

[4] J. C. Slater, Phys. Rev. **84**, 179 (1951).

[5] J. F. Nicholas, Proc. Phys. Soc. (London) **A66**, 201 (1953).

[6] J. Bradley and D. Kahn, Phys. Rev. **143**, 495 (1966).

[7] K. M. Myles and J. B. Darby, Jr., Acta Met. **16**, 485 (1966).

[8] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelly. *Selected Values of Thermodynamics Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).

quasichemical approximation is applied.[9] The entropy factor should decrease the tendency toward clustering (or short-range order) with increasing temperature, and therefore we expect less clustering at higher temperatures rather than the opposite trend observed by Chen.[2] Here, we use specific-heat data to estimate electronic and lattice contributions to the thermodynamic properties and show that the large negative heats of mixing can be explained primarily by electronic contributions. We also observe for the first time that changes in the degree of clustering induced by different heat treatments alter the observed γ value. A preliminary report of this effect has been published elsewhere.[10] There are several calculations of the effects of local order on the electronic structure of alloys.[11–13] The observed change in the electronic specific heat will be discussed in relation to these theories.

The Fermi surface of copper is in contact with the $\{111\}$ Brillouin-zone faces[14,15] and several investigators have studied the effects on the electronic specific heat of alloying dilute concentrations of polyvalent nontransition elements with the noble metals.[16–18] Here we study the effects of alloying dilute concentrations of Pd in Cu. The rigid-band model suggests that the addition of the transition metal should pull the Fermi surface away from the Brillouin-zone boundaries. This reduces the area of contact between the Fermi surface and the Brillouin-zone boundaries, giving rise to an increase in the density of states at the Fermi level. We find, however, no significant increase in the density of states with small Pd additions in conflict with the simple rigid band theory.

II. EXPERIMENTAL PROCEDURE

Alloys of Cu-Pd were prepared from Pd rods (99.99+%) produced by Englehard Industries, Inc. and Cu rods (99.999+%) supplied by American Smelting and Refining Co. Approximately 30–40-g mixtures of the metals were inductively melted in high-purity alumina crucibles under a vacuum of 10^{-5} to 10^{-6} mm Hg. After melting, each alloy was weighed; the average loss in weight corresponded to a few tenths of an atomic per cent and therefore the composition of the alloys was taken to be the initial one prior to melting. The alloys were homogenized for one week at 950 to 1050°C depending upon the composition under a purified argon atmosphere. The high-temperature fcc structure of the α-phase alloys was retained by quenching. To improve quenching conditions the ingots (about $\frac{1}{2}$ in. in diameter and 1 in. in length) were sectioned into quarters along their cylindrical axis. Then the alloys were sealed in vycor tubes under a vacuum of about 10^{-6} mm Hg, held for 90 min at 950°C, and quenched in ice water.

TABLE I. Summary of low-temperature thermodynamic values for the β and β phases of Cu-Pd alloys. Errors: random errors at 95% confidence limit.

At.% Pd	Phase	γ mJ/ moleρK^2	Θ_D°K	A_1 mJ/ mole°K^4	A_2 mJ/ mole°K
1	α	0.692 ± 0.003	340.0 ± 1.3	0.0495	
3	α	0.700 ± 0.004	336.5 ± 1.4	0.0511	
5	α	0.704 ± 0.003	334.6 ± 1.3	0.0519	
6	α	0.699 ± 0.003	332.7 ± 1.2	0.0528	
7	α	0.698 ± 0.003	332.3 ± 1.3	0.6530	
10	α	0.718 ± 0.003	330.1 ± 1.3	0.0541	
15	α	0.736 ± 0.005	328.5 ± 1.4	0.0549	
28	α	0.783 ± 0.004	321.2 ± 1.3	0.0587	
37	β	0.717 ± 0.004	314.9 ± 1.3	0.0627	
39	β	0.576 ± 0.003	302.3 ± 1.3	0.0701	1.46×10^{-3}
41*A*[a]	β	0.563 ± 0.004	296.3 ± 1.2	0.0748	1.03×10^{-3}
41*Q*[b]	α	0.783 ± 0.004	312.5 ± 1.2	0.0638	
43	β	0.573 ± 0.004	293.8 ± 1.2	0.0766	0.917×10^{-3}
45	β	0.583 ± 0.004	294.9 ± 1.2	0.0759	0.769×10^{-3}
58*Q*	α	2.31 ± 0.006	307.5 ± 1.2	0.0671	
58*A*	α	2.31 ± 0.006	308.4 ± 1.2	0.0661	
67.5*Q*	α	3.45 ± 0.008	305.0 ± 1.2	0.0686	
67.5*A*	α	3.40 ± 0.008	305.0 ± 1.2	0.0687	
75*Q*	α	4.32 ± 0.009	302.4 ± 1.2	0.0703	
75*A*	α	4.24 ± 0.009	304.1 ± 1.2	0.0691	
90*Q*	α	7.26 ± 0.016	287.1 ± 1.2	0.0821	

[a] *A*: aged or annealed state. [b] *Q*: quenched state.

At compositions corresponding to the β-phase alloys, this treatment was not sufficient to completely suppress the transformation from the fcc (α phase) to bcc (β phase). A 41-at.% Pd-quenched sample was, however, reasonably pure α and its low-temperature specific heat was also tested. To obtain the β-phase alloys, the homogenized samples were furnace-cooled from 1050°C and subsequently annealed at approximately 20°C below the β-phase boundary for 24 h. Some of the Pd-rich alloys were given additional heat treatments to change the degree of local atomic order. These samples were sealed in evacuated pyrex tubes and aged at 325°C for two weeks.

The calorimetric procedures have been discussed elsewhere.[19] Basically, the calorimeter is of the discontinuous pulse-heating type. Heat transfer from the sample is accomplished with a mechanical heat switch. To check the performance of the calorimeter the heat capacity of 99.999+% Cu (vacuum melted, ASARCO) was measured and the results are

$$\gamma=0.697\pm0.002\ \mathrm{mJ/mole^\circ K^2},$$

$$\Theta_D=342.0\pm1.2^\circ\mathrm{K}.$$

The error limits refer to random errors estimated at

---

[9] R. A. Swalin, *Thermodynamics of Solids* (John Wiley & Sons, Inc., New York, 1962).

[10] Y. Sato, J. M. Sivertsen, and L. E. Toth, Phys. Letters **28**, 118 (1968).

[11] P. A. Flinn, Phys. Rev. **104**, 350 (1956).

[12] R. D. Mattuck, Phys. Rev. **127**, 738 (1962).

[13] R. D. Mattuck, J. Phys. Chem. Solids **23**, 1637 (1962).

[14] A. B. Pippard, Phil. Trans. Roy. Soc. London **A250**, 325 (1957).

[15] D. Schoenberg, Phil Mag. **5**, 105 (1960).

[16] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

[17] J. M. Ziman, Advan. Phys. **10**, 1 (1961).

[18] V. Heine, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

[19] L. E. Toth, Technical Report No. AFOSR-0265, 1968 (unpublished), Defense Documentation No. Ad 671-944.

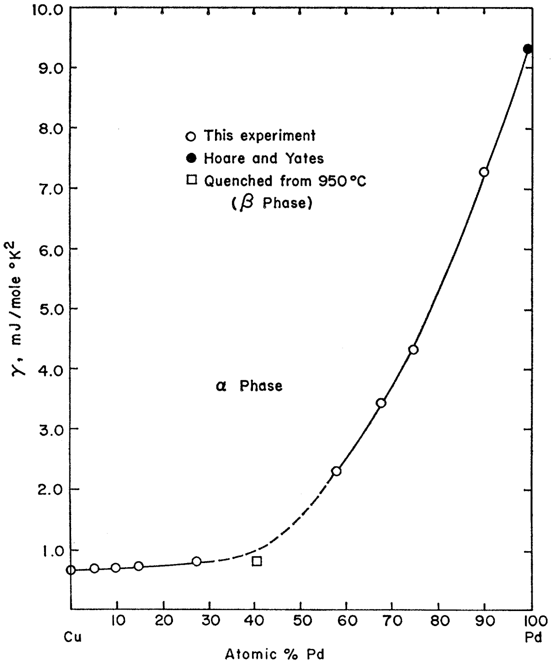

FIG. 1. The dependence of γ on composition in the Cu-Pd system for α-phase alloys. The dotted line indicates the region of stability for the β phase.

95% confidence limits as calculated by the method of least squares. Systematic errors are about ±1% for both γ and Θ_D. These results are in agreement with literature values.[20]

III. EXPERIMENTAL RESULTS

The data were fitted by the method of least squares to the following relationships:

$$C/T=\gamma+A_1T^2 \quad (1)$$

and

$$C/T=\gamma+A_1T^2+A_2T^4. \quad (2)$$

The second relation was used for most of β-phase alloys (except 37 at.% Pd). For the α phase, the coefficient A_2 was insignificant and the γ and Θ_D values were obtained from the first relation. The fitted values of the coefficients together with the Debye temperature deduced from A_1 are listed in Table I.

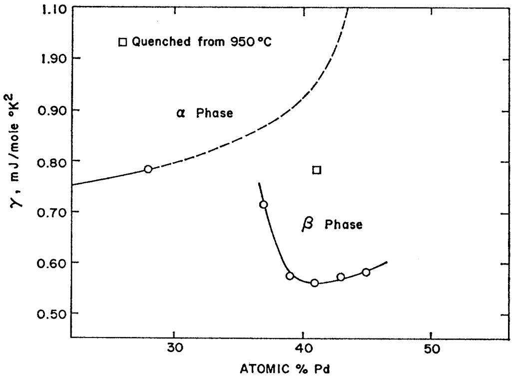

FIG. 2. The dependence of γ on composition in the Cu-Pd system for β-phase alloys.

Figure 1 shows the composition dependence of γ. The broken line in Fig. 1 corresponds to the region where the β phase is stable. The γ values for the β phase behave differently from those of the α phase ,and these differences are shown in more detail in Fig. 2. For the 41-at.% Pd alloy two sets of measurements were made for two different heat treatments, one quenched from 950°C after being held there for 90 min, and the other annealed at 580°C for 24 h. The quenched sample was nearly pure α and the annealed sample nearly pure β as determined by x-ray techniques. The γ value for the α phase was 0.783 mJ/mole°K^2 and the value for the β phase was 0.563. The γ value for α is somewhat smaller than the value expected from the extrapolated variation of γ for the α phase found in other compositions regions. This difference may be due to the fact that the transformation to the β phase cannot be completely suppressed by quenching.[21] All β-phase alloys (annealed) also show slight traces of the fcc structure (α) on x-ray diffraction patterns taken by the back-reflection method.

Details of the dependence of γ upon composition in the dilute Pd region are shown in Fig. 3; the length of bars indicates the uncertainty of each data point due to random errors. The results show that γ values for the dilute alloys are relatively insensitive to the presence of Pd atoms up to about 8-at.% Pd.

The Debye temperatures are plotted in Fig. 4 for both α and β. In Cu-rich alloys Θ_D is sensitive to the Pd concentration in contrast to the behavior of γ.

The results deviate from the Neumann-Kopp rule, negatively below and positively above 40-at.% Pd. The Θ_D value for the quenched 41-at.% Pd alloy is slightly below the extrapolated behavior for α (broken line). This slight difference is probably due to the small amount of β in the sample resulting from the difficulty in suppressing the β transformation.

Coefficients of A_2 (T^5 component) in the specific heats of the β-phase alloys varied systematically with concentration; A_2 decreases with increasing Pd composition (see Table I). The significance of this behavior is not understood. A similar tendency of an upward curvature of C/T versus T^2 has been observed by Montgomery *et al.*[22] for Ag-Pd alloys in the same analogous composition range. They analysed the data by adding a A_3/T term to the right-hand side of Eq. (1); this term is appropriate in cases where localized ferromagnetic inclusions exist. They found, however, no composition dependence of the coefficient A_3. They also suggested that this anomalous specific heat may be

---

[20] D. L. Martin, Phys. Rev. **170**, 650 (1968).

[21] F. W. Jones and C. Sykes, J. Inst. Met. **65**, 419 (1939).

[22] H. Montgomery, G. P. Pells, and E. M. Wray, Proc. Roy. Soc. (London) **A301**, 261 (1967).

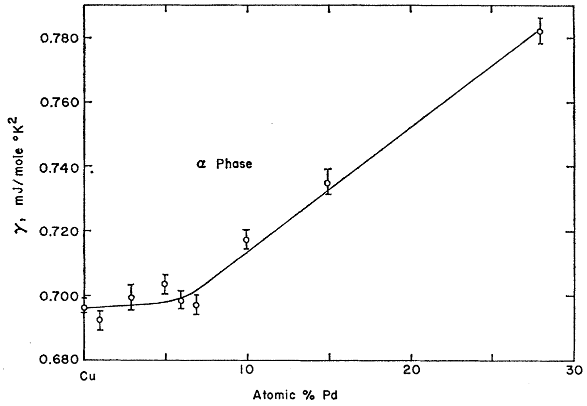

FIG. 3. The dependence of γ in Cu-rich alloys.

due to the contamination by iron impurities. If this is the case then it is not easily understood why this behavior appears in this same concentration range in both the Cu-Pd and Ag-Pd alloy systems and not in other regions of the respective phase diagrams. The disappearance of the anomally on quenching the 41-at.% Pd alloy (Table I) suggests that variations in the atomic configurations may be involved. Although the Ag-Pd system does not have a superlattice structure and exhibits complete solid solutions at room temperature, there is a strong indication that short-range order may exist in this system.[23] Moreover, destruction of short-range order by cold working tends to decrease the A_3 coefficient in this system,[22] also indicating that there are some influences of short-range order on the anomalous specific heat.

IV. DISCUSSION

A. Band Structure

In the rigid-band model it is assumed that the overall band shape is unchanged as a pure metal is alloyed. The addition of Cu to Ni, Ag to Pd, and Au to Pt should in each case add electrons to a partially empty *d*-band of the solvent metal. Figure 1 can be interpreted as showing that in pure Pd there are about 0.6 electrons per atom in the 5*s* band and the same number of vacant states in the 4*d* band. The rapid decrease of γ values as the copper concentration increases is associated with the filling of holes in the *d* band with the *s* electrons of copper. This process continues until the *d* band is completely filled. Beyond this point, corresponding to about 60-at.% Cu, the γ values level off with increasing Cu concentration.

On the basis of a simple collective electron model and a rigid-band model, the electron density of states $N(E)$ for one spin direction may be computed by following the treatment of Hoare *et al.*[24] $N(E)$ and γ are related by the

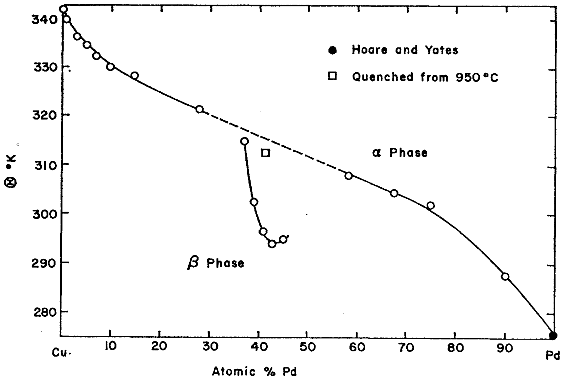

FIG. 4. The variation of the Debye temperature in Cu-Pd alloys.

equation

$$N(E)=3\gamma/2\pi^2k^2. \tag{3}$$

Here γ has been experimentally determined as a function of the mole fraction of Cu, X_{Cu}. To obtain a $N(E)$-versus-E relationship we use a graphical integration:

$$\frac{1}{2}\int_0^{X_{\mathrm{Cu}}}\frac{1}{N(E)}dX_{\mathrm{Cu}}=E_x-E_0\equiv\epsilon. \tag{4}$$

The $N(\epsilon)$-versus-ϵ curve is shown in Fig. 5. The results obtained by Hindley and Rhodes[25] for the Ag-Pd system are also shown for comparison. There are some minor differences in the shape at the tail of the *d* band obtained for Cu-Pd and for Ag-Pd.

While there are doubts about the validity of the rigid-band model, the present results at least provide evidence about the constancy of the e/a ratio necessary

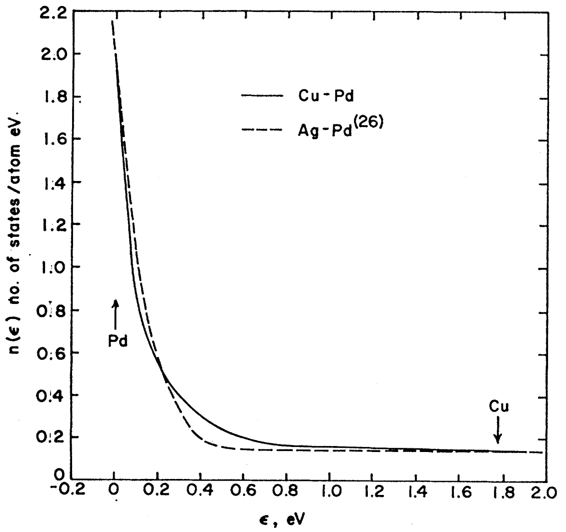

FIG. 5. The variation of $n(\epsilon)$-versus-ϵ curve for Cu-Pd alloys as deduced from the variation of γ with composition in the α phase.

---

[23] W. Chen and M. E. Nicholson, Acta Met. **12**, 687 (1964).

[24] F. E. Hoare, J. C. Matthews, and J. C. Walling, Proc. Roy. Soc. (London) **A216**, 502 (1953).

[25] N. K. Hindley and P. Rhodes, Proc. Phys. Soc. (London) **81**, 717 (1963).

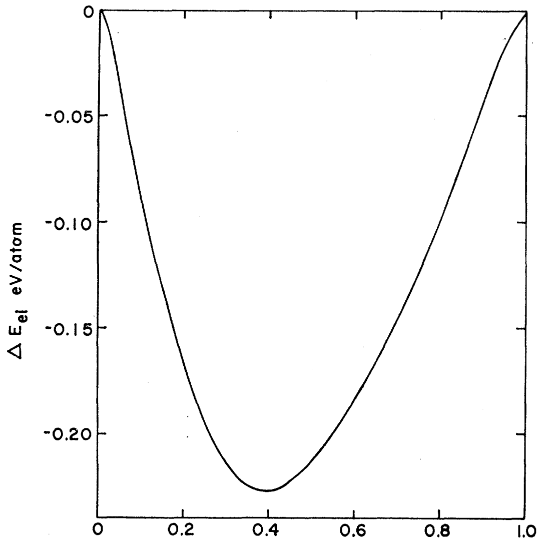

FIG. 6. The election contribution to the heat of mixing as calculated from the $n(\epsilon)$-versus-ϵ curve in Fig. 5.

in both the Cu-Pd and Ag-Pd systems to fill the *d* band. The analysis of the $N(\epsilon)$-versus-ϵ curve (Fig. 5) gives approximately 0.6 holes in the *d* band for Pd. There are, however, several factors which could effect this result. The density of electron states can be considerably different from the free-electron density of states because of the contributions from electron-phonon, electron-electron, electron-magnon, and electron-impurity interactions. Electron-phonon interactions enhance the density of states but it is generally difficult to know by how much, particularly if the metal is a nonsuperconductor.[26] In the case of electron-electron interactions even the sign of the contributions is not certain except for simple metals.[27] The electron-magnon interactions are particularly important for the right-hand side of the transition metal series. For example, the calculation on Pd by Jensen and Andres[28] shows that spin-fluctuation interactions enhance the free electron value of γ by as much as a factor of 8. The electron-impurity interactions discussed by Jones[29] can also make appreciable positive contributions to γ when the Fermi level lies just beyond a high density-of-states peak in the energy band.

B. Thermodynamic Considerations of Cu-Pd Alloys

Electronic and vibrational contributions to the thermodynamic properties may be computed from the specific-heat data. The change in total electronic energy on alloying, ΔE_{el}, was computed from the band structure (Fig. 5) by means of a graphical integration. In Fig. 6, ΔE_{el} is shown as a function of concentration; the change in electronic energy arises from the transfer of electrons from the *s* band of Cu to the empty *d* band of Pd. It is interesting to compare this result with the enthalpy of mixing shown in Fig. 7. The latter curve is for 1000°K while the former corresponds to 0°K. The energy changes for both cases are of the same sign and order of magnitude. In addition, the minimum of the curves takes place at the composition where the *d* band of Pd is just filled. Although the changes are of the same order of magnitude, the estimated electronic changes are about $2\frac{1}{2}$ times more negative than the experimental value of the enthalpy of mixing. Exactly the same behavior has been found in Ag-Pd alloys.[30]

Positive contributions to the enthalpy of mixing will arise from the strain energy due to misfit of atoms with different sizes. The small size difference between Cu and Pd suggests that significant contributions are not likely to arise. The magnetic contribution such as the exchange energy between the atomic magnetic moments associated with Pd atoms has a complex form but is expected to be small.[7] Shimizu *et al.*[31] have shown that the Fermi energy of Pd increases approximately by 0.02 eV/atom as the temperature increases from 0 to 1000°K and therefore the temperature correction of the Fermi energy will not change the result significantly. At

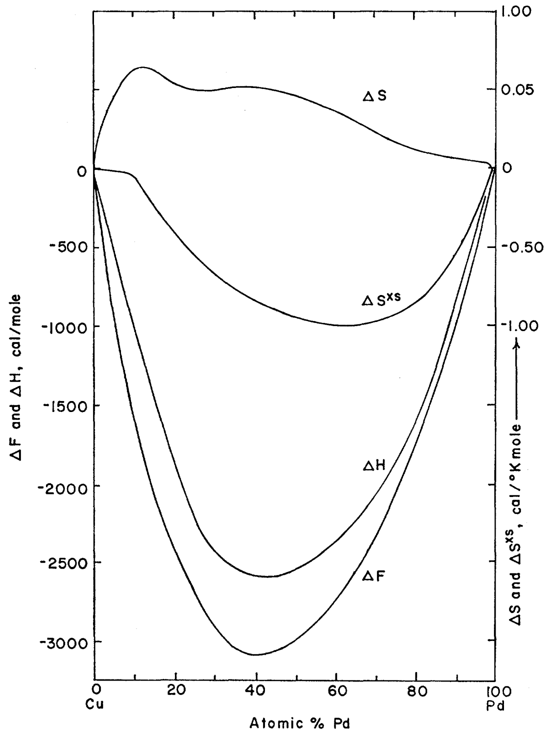

FIG. 7. Thermodynamic functions in the Cu-Pd system at 1000°K (after Hultgren *et al.*, Ref. 8).

---

[26] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[27] J. J. Quinn, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

[28] M. A. Jensen and K. Andres, Phys. Rev. **165**, 545 (1968).

[29] H. Jones, Phys. Rev. **134**, A958 (1964).

[30] J. N. Pratt, Trans. Faraday Soc. **56**, 975 (1960).

[31] M. Shimizu, T. Takahashi, and A. Kastuki, J. Phys. Soc. Japan **18**, 240 (1963).

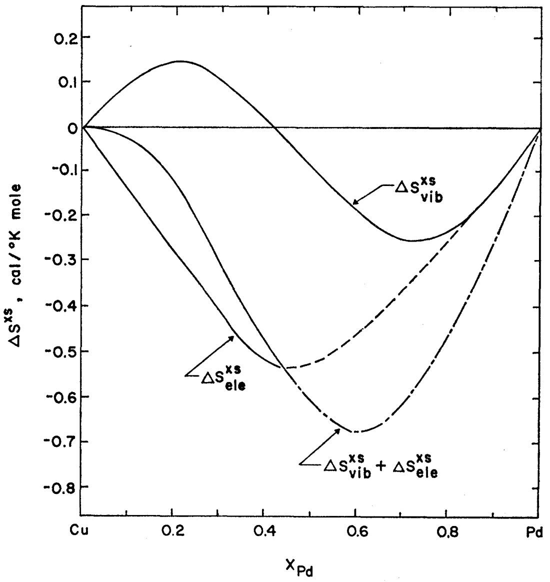

FIG. 8. Excess vibrational and electron entropies at 1000°K as calculated from Θ_D and γ values. The γ value for Pd and Pd-rich alloys were corrected for temperature effects.

1000°K the contribution to the heat of mixing due to corrections in both γ and Θ_D values for the alloy Cu–40-at.% Pd is estimated to be about −400 cal/g atom.

Close agreement between the estimated and observed ΔH_{mix} curves should not be expected from the simplified model used here. Nevertheless, the results suggest that the change in the electronic structure upon alloying may be the most important factor for explaining the observed enthalpy of mixing, and that configurational contributions are smaller. If this is the case it may be difficult to predict from the enthalpy of mixing which type of local order dominates the atomic configuration in this system. Thus the large negative values for the heat of mixing may not necessarily mean the presence of short-range order. This behavior may explain why Chen[2] found evidence for clustering from x-ray diffuse measurements.

Excess vibrational and electronic entropies were computed from the following equations:

$$\Delta S_{\mathrm{VI}B}{}^{\mathrm{xs}}=3R\ln\frac{\theta_{\mathrm{Cu}}{}^{X_{\mathrm{Cu}}}\theta_{\mathrm{Pd}}{}^{X_{\mathrm{Pd}}}}{\Theta_D} \qquad (5)$$

and

$$\Delta S_{\mathrm{el}}{}^{\mathrm{xs}}=\gamma^{\mathrm{ex}}T=[\gamma_{\mathrm{alloy}}-(X_{\mathrm{Cu}}\gamma_{\mathrm{Cu}}+X_{\mathrm{Pd}}\gamma_{\mathrm{Pd}})]T. \qquad (6)$$

Here Θ_D, θ_{Cu}, and θ_{Pd} are the Debye temperature of the alloy, pure Cu, and pure Pd, respectively. In order to compare the total excess entropy, the sum of $\Delta S_{\mathrm{VI}B}{}^{\mathrm{xs}}$ and $\Delta S_{\mathrm{el}}{}^{\mathrm{xs}}$, to other experimental values of $\Delta S_{\mathrm{total}}{}^{\mathrm{xs}}$ determined at 1000°K (see Fig. 7), it is necessary to correct Eqs. (5) and (6) for the effects of temperature. For several metals the experimental values of the electronic contribution to the specific heat at high temperatures are considerably smaller than those calculated from γ values measured at low temperatures. A particularly striking example is provided by Pd. Values of $\Delta S_{\mathrm{el}}{}^{\mathrm{xs}}$ at 1000°K calculated from γ values are about four times higher than experimental high-temperature values.[32] Shimizu *et al.*[31] and Hindley and Rhodes[25] have calculated numerically the electronic contribution to the specific heat of Pd over a wide temperature range (0 to 1500°K), using the density of states obtained from low-temperature specific heats of Ag-Pd[33] and Rh-Pd.[34] A temperature correction is necessary for the electronic contribution at high temperatures for such cases where the Fermi energy is located on the sharp peak of the density of states. For Cu-rich alloys (up to 50-at.% Pd) where the Fermi energy is located beyond the peak the temperature correction is not significant. In the present calculation, the entropy of pure Pd at 1000°K was taken from the results of Hindley and Rhodes.[25] Pd-rich alloys the excess entropy was extrapolated from the value corresponding to 50-at.% Pd to pure Pd (the broken line in Fig. 8).

The sum of the vibrational and electronic entropy is shown in Fig. 10. The resulting curve indicates that the general shape of the estimated entropy agrees quite well with that of the experimental one (Fig. 7). The minimum in the estimated curves occurs at about 60-at.% Pd while that of the experimental data takes place at 65-at.% Pd. The difference is small considering the approximations used for the estimation. Since the magnetic contribution to the excess entropy is negative,[35] the inclusion of this contribution would improve

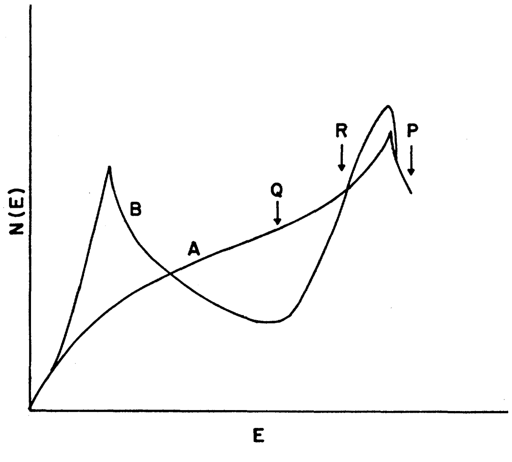

FIG. 9. Schematic diagram of the $n(\epsilon)$-versus-ϵ curve for a disordered alloy (curve *A*) and an alloy with long-range order [after Nicholas (Ref. 5)]. The point *Q* probably corresponds to the difference between the disordered α alloys and the ordered β alloys in the Cu-Pd system.

---

[32] See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953).

[33] F. E. Hoare and B. Yates, Proc. Roy. Soc. (London) **A240**, 42, (1957).

[34] D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) **A257**, 250 (1961).

[35] K. M. Myles, Acta Met. **13**, 109 (1966).

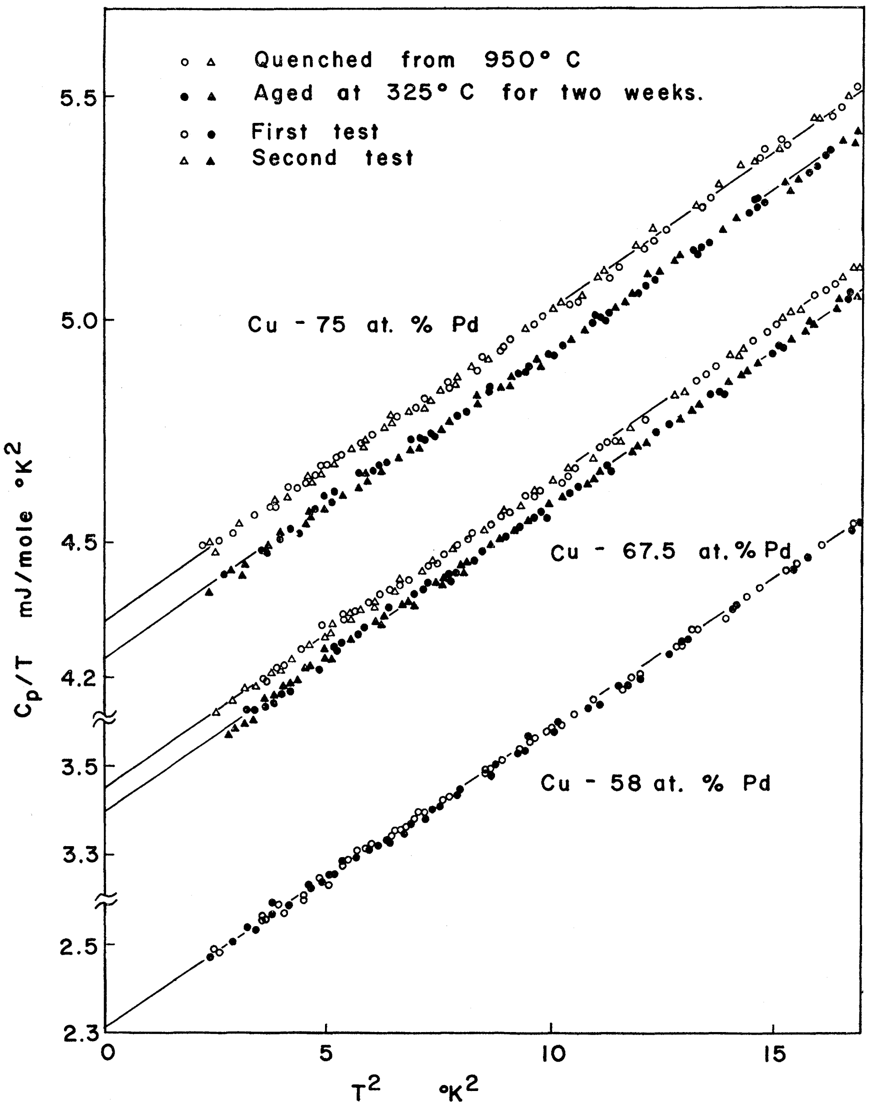

FIG. 10. In Pd-rich alloys local clustering exists (Ref. 2) and the amount of clustering is temperature-dependent. Quenched samples retain more local clustering than aged samples (Ref. 2). Slight differences in the γ values for the two states of clustering are observed in Cu–75-at.% Pd and Cu–67.5-at.% Pd alloys.

the agreement. The bulk of the excess entropy, may be attributed to the contributions arising from electronic, vibrational and magnetic origins, and the configurational contribution, therefore, may be small as expected from the results of x-ray diffuse scattering.[2]

C. Dilute Cu-Pd Alloys

The results of γ versus concentration in Cu alloys with small concentrations of Pd (Fig. 3) are in conflict with a simple rigid-band model. Since the Fermi surface is in contact with the {111} faces of the Brillouin zone, alloying Pd in Cu should result in a more spherical Fermi surface and increased γ values. Another positive contribution to γ values with Pd additions is expected from the impurity-electron interactions discussed by Jones.[29] No increase in γ with Pd concentration in the dilute Cu-Pd alloys is observed, however, Similar discrepancies between observed and theoretical predictions are found in the data for other Cu-based alloys.[36,37] Electron-magnon contributions may not be important for these alloys since the concentration of Pd is too small to give rise to the significant exchange interactions with the neighboring atoms. We expect that the electron-phonon enhancement should be almost constant in the dilute alloys. The contribution due to the electron-electron interaction is estimated to be small.[38] Thus, we may expect that the observed change in γ reflects at least qualitatively the change in the density of states at the Fermi surface.

---

[36] L. L. Isaacs and T. B. Massalski, Phys. Rev. **138**, A134 (1965).

[37] G. A. Sargent, L. L. Isaacs, and T. B. Massaski, Phys. Rev. **143**, 420 (1965).

[38] N. W. Ashcroft and J. W. Wilkins, Phys. Letters **14**, 285 (1965).

D. β-Phase Alloys

Values of γ for β-phase alloys are considerably different from those of the α phase (Fig. 2). In analogous alloy systems, strong variations of γ because of the occurrence of long range order has been reported by Roessler and Rayne[39] in CuPt and by Goldman[40] in Ni_3Mn. In contrast, the formation of long range order had little effect on γ in Cu_3Pd[41] and Cu_3Au.[42] In CuPt the ordered state has atomic configurations in which atoms of two kinds are arranged on alternate (111) planes so that the number of nearest-neighbor atoms of the ordered structure does not differ from that of the disordered.[43] Hence, the ordinary explanation of ordering, the preference of an atom to be surrounded by neighbors of the other type does not necessarily apply.

The effect of superlattice formation on the electronic structure was considered by Muto,[3] Slater,[4] and Nicholas.[5] When a superlattice forms in an alloy, new Brillouin-zone boundaries are formed corresponding to the extra Bragg reflection, giving rise to a reduction in the size of the basic Brillouin zone. The introduction of the boundaries can lower the electronic energy of the alloy by interacting with the electrons near the Fermi surface. In a free-electron approximation the density of states will be parabolic (Fig. 9, curve A), where a cusp corresponds to the distortion of the Fermi surface due to the contract with the first Brillouin zone boundaries. Since in pure Cu the Fermi surface just touches the boundaries, it is probably located at the position indicated by P in the figure. According to a simple rigid band model alloying Cu with Pd will eventually pull the Fermi surface away from the boundaries and reduce the Fermi energy. At a composition corresponding to the β phase (40-at.% Pd), the Fermi surface of the α phase may be taken as spherical in shape and we qualitatively locate it at point Q of curve A in Fig. 9. In our measurements there was no indication of a peak in γ corresponding to the cusp, where the Fermi surface breaks away from the zone boundaries. On superlattice formation the appearance of new zone boundary will split the energy band (Fig. 9, curve B).[15] Hence if the Fermi surface is located at point Q, we should expect considerable reduction in the density of states, whereas little change is expected in the value at the point R (which may be the case for Cu_3Pd).

There may be masking effects on γ due to the electron-phonon, the electron-electron, and the electron-magnon interactions. The change in atomic configuration on ordering may induce changes in these interactions. This may give rise to an additional change in γ.

The Debye temperature of Cu_3Au,[42] CuPt,[39] and Ni_3Mn[40] increases with the formation of long-range ordering which is in contrast to the present results (Fig. 4). The value of the Debye temperature obtained from low-temperature specific heats is related to the elastic constants. The observed decrease in the Debye temperature of the Cu-Pd alloys on ordering is in agreement with the decrease in Young's modulus,[44] whereas the Young's modulus of Cu_3Au[45] and Ni_3Mn[46] and the Brinnel hardness of CuPt[47] increase on ordering.

E. Pd-Rich Alloys

In Pd-rich alloys there is a tendency towards clustering (3). The amount of clustering is dependent upon the temperature and various degrees of clustering can be retained at room temperature by aging and quenching from different temperatures. We have observed a small variation in γ between the quenched and the aged states (see Fig. 10). A similar variation in γ has been observed in the Fe-Pd system.[48] Since similar heat treatments induce large changes in the short-range order coefficient α,[2] we believe that the changes in γ are due to changes in local atomic order.

The observed decrease on aging in the γ values for the 67.5 and 75-at.% Pd alloys is consistent with the changes in magnetic susceptibility.[2] For the 58-at.% Pd alloys the x-ray diffuse scattering studies show that the local order is very nearly random in both the quenched and aged states. Thus, little change in the electronic specific heat is expected for this alloy.

Flinn[11] and Mattuck[12,13] considered the effect of local order on the electronic structure of alloys. Mattuck[13] using a tight-binding approximation, derived the following expression for the density of states as a function of α:

$$N(\epsilon,\alpha_1)\sim\frac{\epsilon^{1/2}}{X_A[1+\alpha_1(X_A{}^{-1}-1)]^{3/2}},\tag{7}$$

where X_A is the mole fraction of a component A. Equation (7) shows that as α_1 changes from negative to zero to positive values (corresponding to short-range order to random to clustering), $N(\epsilon,\alpha_1)$ lowers in value.

If the results of low-temperature specific heats are combined with those of x-ray diffuse scattering, then Mattuck's prediction is in contradiction to our observations that $N(\epsilon,\alpha_1)$ decreases as clustering decreases on aging a quenched sample. A similar conflict between theory and experimental data has been found for a Fe-Pd alloy, in which $N(\epsilon,\alpha_1)$ decreases as short range

---

[39] B. Roessler and J. A. Rayne, Phys. Rev. **136**, A1380 (1964).

[40] J. E. Goldman, Rev. Mod. Phys. **25**, 108 (1953).

[41] P. N. Stetgenko and Y. N. Avksentjev, Ann. Acad. Sci. Fennicae Ser. A. VI, No. **210**, 226 (1966).

[42] J. A. Rayne, Phys. Rev. **108**, 649 (1957).

[43] C. B. Walker, J. Appl. Phys. **23**, 118 (1952).

[44] W. Köster, Z. Metalk. **32**, 145 (1940).

[45] S. Siegel, Phys. Rev. **57**, 537 (1940).

[46] T. Fukuroi and Y. Shibuya, Sci. Rep. Res. Inst. Tohoku Univ., Ser. A **2**, 829 (1950).

[47] L. Nowack, Z. Metalk. **22**, 94 (1930).

[48] Y. Sato, A. Joshi, J. M. Sivertsen, and L. E. Toth, J. Phys. Soc. Japan **26**, 861 (1969).

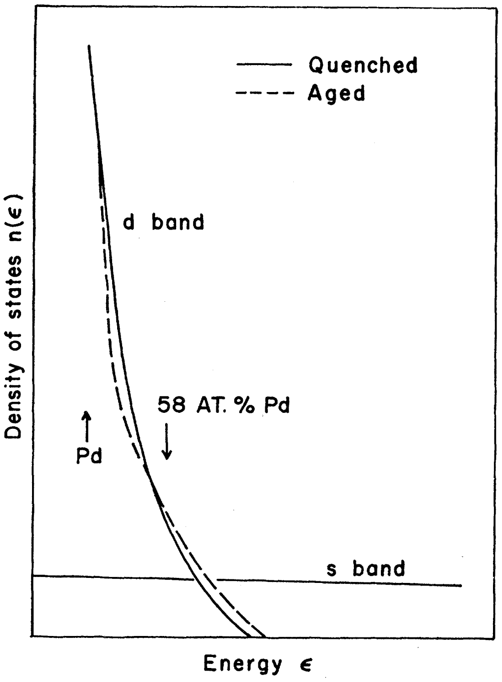

FIG. 11. A schematic diagram depicting the variation of the $n(\epsilon)$-versus-ϵ curve in Cu-Pd alloys due to differing amounts of local clustering.

order increases on aging.[48] Since the observed γ reflects contributions from several interactions, such as electron-phonon and electron-electron, the effects of these contributions on the change in γ should also be taken into consideration.

Chen[2] has observed that the residual resistivity of 75-at.% Pd, Cu-Pd alloy is reduced about 2% on aging at 300°C for two weeks after being quenched from 950°C, and that the magnetic susceptibility decreases by about 4% due to this heat treatment. If it is assumed that the electrical resistivity of a transition metal alloy is mainly due to transitions in which the electrons jump from the s to the empty d band[49] the observed change in the residual resistivity with aging is due to the change in the density of states in the d band. The sign and magnitude of the observed resistivity changes are in agreement with the present results on the change in γ due to aging. Figure 11 schematically illustrates the change in the density of states in the d band due to different heat treatments.

V. CONCLUSION

The results of low-temperature specific heats provide an interesting correlation between the thermodynamic properties and the band structure of Cu-Pd alloys. The results demonstrate the importance of electronic contributions to the thermodynamics properties associated with the formation of transition metal alloys.

The calculated band structure of Cu-Pd alloys agrees, in general, with that of Ag-Pd alloys. The rigid-band hypothesis can be applied for interpretation of the results except in the case of dilute Pd alloys, where the present results indicate the Fermi surface of Cu is unaffected by the presence of Pd atoms up to moderate concentrations.

The observed decrease in the γ values on superlattice formation is attributed to the splitting of the energy band. The position of the Fermi level in the energy band may be a dominant factor responsible for the change in γ. The energy of the ordered state is lowered by the Fermi-surface–Brillouin-zone interaction compared with the disordered state. The change in the Debye temperature is consistent with the change in the elastic properties upon order-disorder transformations.

The effects of local order on low-temperature specific heats show that the γ values of quenched alloys decrease upon aging. The results, which are consistent with other measurements, i.e., electrical resistivity and magnetic susceptibility, are interpreted as a slight modification taking place in the d band due to local atomic rearrangements. At present, we are not able to establish a general relation between local order and the density of states.

Note added in manuscript. Since the completion of this work, it has come to our attention that Wallden[50] has recently measured the optical properties of Cu-rich Cu-Pd alloys and claims that "the 4d electrons of Pd are contained in a resonant bound state that is located 1.2 eV and further below the Fermi level, overlapping the Cu 3d band." His results may help explain why the rigid-band approximation cannot be applied to the Cu-rich alloys.

ACKNOWLEDGMENTS

One of the authors (L.E.T.) thanks the National Science Foundation for supporting this research. The other two (J. M. S. and Y. S.) gratefully acknowledge the support of the U. S. Office of Naval Research.

---

[49] N. F. Mott and H. Jones, *The Theory of Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1936).

[50] L. E. Wallden, Solid State Commun. **7**, 593 (1969).