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Effect of Heat Treatment on the Specific Heat of Cu–40-at.% Ni below 3°K

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Assuming that clusters contribute to the specific heat as an Einstein term (represented by a Thirring expansion), it is found that (a) the magnitude of the cluster term (proportional to the *number* of clusters) is independent of quenching temperature for quenching temperatures above about 550 °C and nearly doubles for some lower quenching temperatures, and (b) the electronic-specific-heat coefficient shows a strong dependence on the magnitude of the cluster term and the Debye temperature a weak dependence. The first observation (a) may be interpreted as showing (i) that cluster formation only occurs at temperatures below about 550 °C, (ii) that cluster formation during quenches from higher temperatures occurs because an excess of thermally generated lattice vacancies is then present which facilitiates atomic movement, (iii) either the number of excess vacancies available is independent of quenching temperature (owing, for example, to aggregation effects) or cluster formation during quench is limited by the distance of atomic movement required, and (iv) it is impossible to inhibit cluster formation in a sample of the size used (50 g) with the present quenching techniques. The second observation (b) suggests a way of extrapolating to the unclustered state. It may also indicate that the Einstein term is not the best representation for the cluster specific heat.

I. INTRODUCTION

Copper-nickel alloys have been of interest for many years[1] because (a) nickel has an unfilled *d* band and is ferromagnetic whereas copper has a filled *d* band and (b) they form a continuous range of solid solutions. Thus it is possible to investigate the transition from ferromagnetism to paramagnetism in this alloy system. However, the situation is complicated by the tendency of nickel atoms to form clusters. Thus the solid solution may not be homogeneous which makes the interpretation of most measurements more difficult. The author's interest in the problem was aroused by a recent controversy[2] regarding the interpretation of optical measurements in Cu-Ni alloys, in particular the effect of heat treatment on possible clustering. It was suggested that quenching from a high temperature should inhibit cluster formation. This seemed improbable because recent specific-heat measurements[3] (confirming earlier observations by other techniques[4]) on alloys showing order/disorder transformations could be interpreted as showing that considerable ordering occurs on a quench from high temperatures, whereas quenching from a temperature just above the order/disorder phase boundary minimizes the ordering. This is because an excess of thermally generated lattice vacancies will facilitate atomic movement. The magnitude of this effect obviously depends on the number of effective equilibrium lattice vacancies present at the disordering temperature together with other factors. Nevertheless, it was thought that a similar effect should be seen in Cu-Ni alloys as a dependence of the *number* of clusters on quenching temperature. Clusters have a large effect on the low-temperature specific heat so this is a suitable technique to use.

The earliest theory of the specific heat of superparamagnetic clusters was given by Schröder and Cheng[5] and later developments are surveyed by Hahn and Wohlfarth[6] who also summarize the evidence that specific-heat anomalies seen in various alloy systems are, in fact, the result of such clusters. A crude way of explaining the cluster specific heat is to remember that a magnetic dipole of spin S in a local field gives rise to a Schottky anomaly in the specific heat as the energy levels are repopulated with increasing temperature. (The field may, in fact, be merely a convenient way of representing local anisotropy.) As $S \rightarrow \infty$ (corresponding to an infinitely large cluster of similarly oriented dipoles) it can be shown that the anomaly becomes temperature independent at the lowest temperatures (because the separation between energy levels is infinitely small) and falls off in the usual way as $(1/T^2)$ at high temperatures. Because S is not infinite, the specific heat will fall to zero at the absolute zero. However, a region where the specific heat is independent of temperature may still occur and an Einstein specific heat might be a good approximation to the cluster specific heat up to the temperature where the high-temperature "tail" becomes significant. The temperature-independent specific heat is of magnitude k (Boltzmann's constant) per cluster.

The present measurements (in the range 0.4–3 °K) appear to show a temperature-independent term in the specific heat above about 1 °K but a significant decrease in this term occurs at lower temperatures. In order to use all the measure-

TABLE I. Chemical-analysis results.

Sample	Weight range (g)	Composition (at.% Ni)	Analysis mean	Atomic weight from composition analysis	Difference of atomic weight from nominal (%)	Impurities ppm by weight				
						Semiquantitative spectrographic analysis		Quantitative spectrographic analysis		
						Mg	Ag	Fe	Mn	Si
1	48.24–44.76	40.321	40.324	61.592	−0.025	0.05–0.5	⋯	4.8	⋯	0.3
		40.326				0.07–0.7		5.1	⋯	0.4
2	53.05–44.78	40.066	40.044	61.606	−0.003	0.07–0.7	1.0–12.0	5.7	0.05	1.3
		40.021				0.1–1.0	1.0–12.0	3.7	0.04	1.0

ments in the analysis, the cluster term in the specific heat ($C_{\rm cl}$) has been represented by a Thirring series[7]:

$$C_{\rm cl}=A(3)+A(2)/T^2+A(1)/T^4+\cdots\ .$$

Three terms are found to give an excellent fit to the present specific-heat results.

The alloy composition chosen for investigation (40-at.% Ni) is safely within the paramagnetic region (which extends up to about 42-at.% Ni)[8] but still within the region where the cluster term in the specific heat is large and where magnetic measurements show Ni-rich clusters to be present.[9] Previous specific-heat measurements on Cu-Ni alloys[8,10–12] have not included a detailed investigation of the effect of quenching temperature on the results and have often been on relatively impure samples containing considerable amounts of iron impurity which is believed to act as a nucleus for cluster formation,[13] with approximately one iron atom per cluster. In the present work it has been possible to reduce the iron impurities to about 5 ppm.

II. EXPERIMENTAL

Two samples were used, the first being accidentally destroyed during heat treatment. The copper used for both samples was ASARCO (99.999%). The nickel used for the first sample was Koch-Light sponge (99.995%) and for the second was Koch-Light rod (99.998%). The components, in an alumina crucible, were melted under high vacuum (by external resistance heating) and chill cast into a heavy copper mold, producing a disk about 2.5-cm diameter and ~1 cm thick. Analysis results from each end of both samples are given in Table I. It will be noted that, despite the greater nominal purity of the nickel rod, the second sample is slightly less pure than the first. However, in both cases the transition-metal impurity is at a fairly low level (~5 ppm). All calculations were done using the nominal atomic weight. The heat-treatment history of each sample is given in Table II. Before and after each heat treatment the samples were cleaned with dilute nitric acid, washed with distilled water and methanol, and pumped under vacuum for some time. Some trouble was experienced with porosity in the "pipe" area, and if stains remained after repeated cleaning a small amount of sample was removed by turning. These cleaning procedures account for the range of sample weights shown in Table I. For heat treatment the sample was placed in an alumina crucible and sealed, under high vacuum, in a quartz tube. Quenching was performed by dropping the quartz tube from the furnace into water and quickly breaking the tube with a hammer while immersed.

The specific-heat measurements were made in an apparatus described previously.[14] In the present paper all error limits used will be 95% confidence limit derived from the statistical analysis. The total probable error is estimated[14] as 0.4% plus the 95% confidence limit plus error arising from uncertainty in sample composition.

III. RESULTS

The specific-heat results were fitted, by the least-squares method, to the relation

$$C_p=A(1)/T^4+A(2)/T^2+A(3)+A(4)T+A(5)\,T^3\ . \quad (1)$$

The sample thermal history and corresponding values of $A(N)$ are given in Table II. The low-temperature limiting value of the Debye temperature (Θ_0^c) is obtained from the relation $\Theta_0^c=[464.34/A(5)]^{1/3}$. The raw specific-heat data is shown in Fig. 1 as percentage deviation from the five-term fitted relation for each run [except for runs 6 and 7 which are shown as deviations from the fit of both runs combined (Table II)]. The small systematic deviations probably represent temperature scale errors and are the same as those obtained for measurements on pure metals with the same apparatus.[14] Thus the fit of results to Eq. (1) can be considered excellent. Figure 2 summarizes the results.

IV. DISCUSSION

In order to investigate the effect of time held at the quenching temperature, three runs were made

TABLE II. Heat-treatment details and specific-heat results.

Sample	Run	Heat treatment	Least-squares-fit coefficients – (C_p in μcal/°K g atom) A(1)	A(2)	A(3)	A(4)	A(5)	Θ(°K)	Symbol
1	1	Chill cast under high vacuum. 5 day at 975 °C, 11 day at 1150 °C. Slow cool.	3.4 ± 0.8	−88.6 ± 8.4	1258 ± 32	769 ± 25	17.8 ± 2.1	297^{+13}_{-11}	+
	2	18 h at 570 °C. 3-h cool to 392 °C Quench.	3.1 ± 1.6	−87.3 ± 15.4	1276 ± 56	759 ± 43	24.2 ± 3.8	268^{+16}_{-13}	×
2	1	Chill cast under high vacuum. 50 day at 975–930 °C. 1-day cool to 650 °C. Quench.	2.4 ± 2.2	−30.6 ± 17.4	748 ± 52	878 ± 37	12.2 ± 3.1	336^{+34}_{-24}	○
	2	4 day at 880 °C. 5-h cool to 550 °C, 16-h hold at 550 °C. Quench.	1.4 ± 0.7	−27.2 ± 6.1	768 ± 21	876 ± 16	11.8 ± 1.4	340^{+14}_{-12}	□
	3	19 h at 1100 °C. Quench.	1.1 ± 0.7	−21.5 ± 6.8	702 ± 25	881 ± 19	12.8 ± 1.7	332^{+16}_{-13}	△
	4	18 h at 1050 °C, 5-h cool to 975 °C and hold 3 day. 8-h cool to 500 °C. Switch off furnace (~17-h cool to room temperature.	0.4 ± 0.8	−45.7 ± 7.9	1057 ± 28	819 ± 22	12.3 ± 1.9	336^{+19}_{-16}	▽
	5	6 day at 1050 °C, transfer to furnace at 750 °C, hold 1 day. Quench.	0.5 ± 0.7	−15.7 ± 6.8	691 ± 24	897 ± 18	10.7 ± 1.6	351^{+19}_{-16}	◇
	6	21 h at 850 °C. Quench.	0.6 ± 0.7	−17.3 ± 6.7	709 ± 24	882 ± 19	14.2 ± 1.7	320^{+14}_{-12}	◮
	7	Hold 18 day at 20 °C.	0.4 ± 0.6	−15.2 ± 5.4	692 ± 20	900 ± 15	10.0 ± 1.4	359^{+18}_{-15}	⧨
	6,7		0.5 ± 0.7	−16.1 ± 6.8	700 ± 24	891 ± 19	12.1 ± 1.7	337^{+17}_{-14}	
	8	6 day at 1050 °C. 9-h cool to 400 °C, 14-h cool to 380 °C. Quench.	2.5 ± 0.7	−75.9 ± 7.1	1222 ± 25	719 ± 19	26.2 ± 1.7	261^{+6}_{-5}	⦶
	9	6 day at 1050–1100 °C, 2-day cool to 620 °C, 3-day cool to 600 °C, hold 11 day. Quench.	1.0 ± 0.5	−20.7 ± 4.6	716 ± 16	883 ± 13	12.4 ± 1.1	335^{+10}_{-9}	●
	10	3 cycles 1050 °C to below 500 °C (owing to controller and power failures), 2½ day at 1020 °C, 3-h cool to 505 °C, 10-day hold. Quench.	1.8 ± 1.4	−39.6 ± 13.8	909 ± 49	797 ± 39	21.3 ± 3.4	279^{+16}_{-13}	■

TABLE II. (*Continued*)

Sample	Run	Heat treatment	Least-squares-fit coefficients $-(C_p$ in μcal/°K g atom) $A(1)$	$A(2)$	$A(3)$	$A(4)$	$A(5)$	Θ(°K)	Symbol
	11.	3 day at 1050 °C, 7–h cool to 460 °C, 7–day cool to 405 °C, 7–day hold. Quench.	0.6 ± 0.6	-47.9 ± 6.0	1065 ± 21	809 ± 17	14.9 ± 1.4	315^{+11}_{-10}	◆

Error limits are 95% confidence limits from the statistical analysis. 1 cal = 4.186 J.

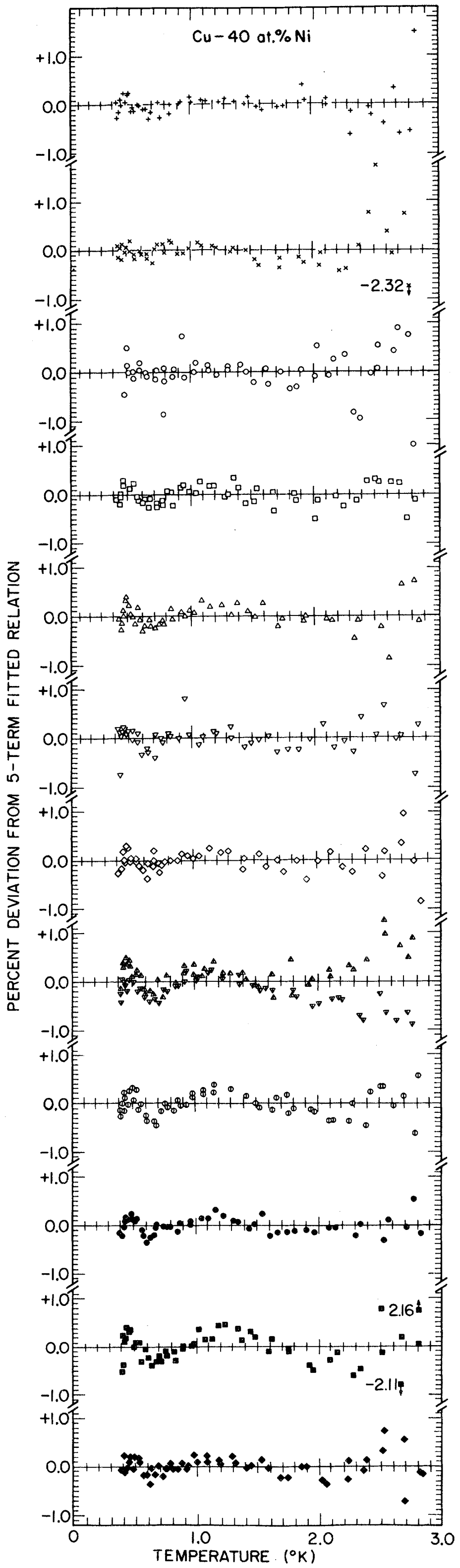

FIG. 1. Deviations of the individual results from the five-term fitted relation. The symbols are identified in Table II. Runs 6 and 7 are plotted as deviations from a combined fit of both runs.

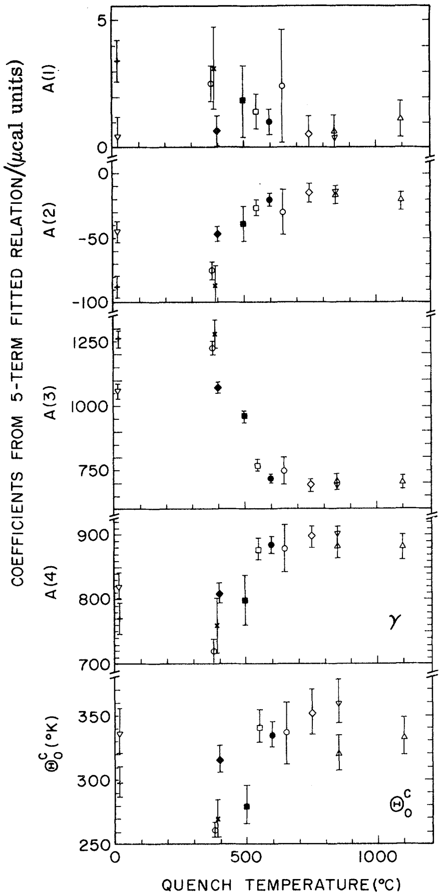

FIG. 2. Dependence on quenching temperature of the terms in the five-term fitted relation.

after a lengthy hold before quenching (solid points). In the region where clustering is occurring such a hold might tend to decrease the magnitude of the cluster term since the *number* of clusters tends to decrease as clusters grow larger. Such an effect is, in fact, seen. Another control experiment (sample 2, run 7) was made to determine the effect of holding at room temperature. There may be a slight effect but, since all other runs were made shortly after quenching, it appears that results should not be significantly affected.

It will be initially assumed that the fitted equation (1) is a correct representation of the results. Another possibility will be mentioned later.

The primary objective of this work was to measure the cluster specific heat as a function of quenching temperature. The temperature-independent term $A(3)$ will be considered (Fig. 2). It will be seen that for quenches of 550 °C and above this term is essentially independent of quenching temperature, whereas it is significantly larger for all lower quenching temperatures and slow cools. This may be taken to show that the miscibility gap for the present composition has a maximum at about 500 °C. This critical temperature for clustering is considerably higher than some estimates including the recent diffuse neutron-scattering measurements of Mozer, Keating, and Moss[15] (~ 250 °C) who summarize previous work. However, the present result agrees rather closely with figures deduced from an internal friction study by Dey[16] and with the electrical-resistance measurements of Schüle and Kehrer[17] who conclude that cluster formation occurs in the range 350–600 °C.

[Another possible explanation for the increase of $A(3)$ for quenching temperatures below 550 °C would be that more vacancies suddenly become available for promoting clustering here (see following paragraph). The explanation given previously is preferred since there is other experimental evidence to support it. The conclusions from the neutron-scattering work[15] are not direct and, as discussed later, there may be a distinction between the high-temperature limits of magnetic and chemical clustering.]

The constant value for $A(3)$ for quenching temperatures of 550 °C and above is rather surprising. In a simple-minded theory an increase with increasing temperature might have been expected as a result of the increased number of lattice vacancies in equilibrium at the quenching temperature (and which, during the quench, facilitate atomic movement towards clustering below the critical temperature for clustering). In fact the number of vacancies available may be reduced by aggregation effects[18] (which in turn produce extended sinks), and the distance of atomic movement required to produce clusters is much greater than required for the ordering effects discussed in Sec. I.

The terms [$A(1)$ and $A(2)$] taken to represent the decrease in the cluster term at low temperatures have the signs expected for a Thirring expansion.[7] The ratios $A(2)/A(3)$ and $A(1)/A(3)$ are not constant. This may result to some extent from the varying characteristic temperature of the clusters and it may also reflect other contributions to these terms. Thus there might be contributions from the nuclear specific heat of magnetic[19] or nuclear quadrupole[20] origin.

In the "classical" region each cluster contributes a specific heat of magnitude k. Hence the range of $A(3)$ observed corresponds to cluster numbers of the order 3×10^{20} per 6×10^{23} atoms of alloy. For a Cu-Ni alloy containing 40-at.% Ni, van Elst, Lubach, and van den Berg[21] have estimated (from magnetic measurements) a magnetic moment of about 60 μ_B per cluster and about 0.17 μ_B for an isolated atom. Hence, very roughly, each cluster might contain 300 atoms, suggesting that 10–20% of all atoms are in clusters. Other estimates[9] of about 10 μ_B per cluster with a cluster concentration of 0.17% suggest a larger number of smaller clusters with a similar total of atoms in clusters.[21a]

There has been discussion whether the clusters are purely magnetic[22] or whether chemical clustering of nickel atoms is required. In the present discussion the latter has been assumed as being consistent with the effect of heat treatment. Other workers have come to the same conclusion for different reasons.[9] It has been shown[23] that an anomalous contribution to the electrical resistivity of Cu-Ni persists up to about 350 °C (independent of concentration over a wide range). This is very close to the Curie temperature of pure nickel and probably marks the high-temperature limit of magnetic as distinct from chemical clustering. Perhaps this is why some authors have obtained a relatively low value for the miscibility gap maximum in these alloys.

Consider now the electronic specific heat [$A(4)$]. In Fig. 3 this has been plotted against the main cluster term $A(3)$. (The straight line is a least-squares fit with intercept 1059 at zero clustering.) It will be seen that there is a strong dependence, the electronic specific heat apparently being decreased by clustering. The simplest explanation of this is obtained by noting that the electronic specific heat of the components of the alloy (i.e., complete segregation) is about 15% less than the maximum observed for the clustered alloy. This observation might be taken to support the clustering hypothesis. (Theory[6] suggests that clustering might result in a small contribution to the specific heat which is linear in temperature, but the magnitude of this term is expected to be small.)

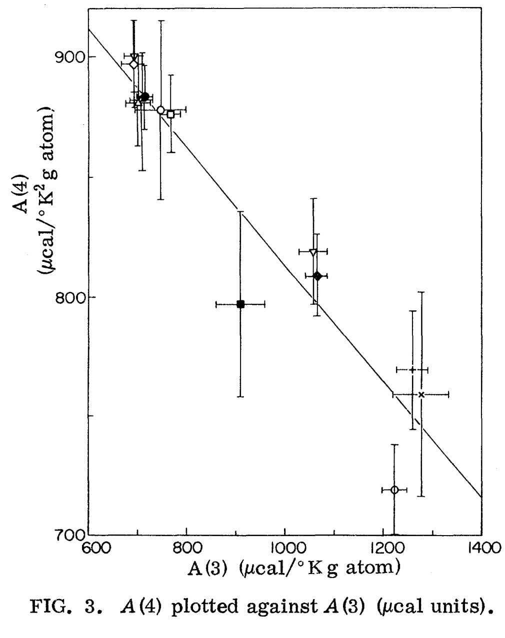

FIG. 3. $A(4)$ plotted against $A(3)$ (μcal units).

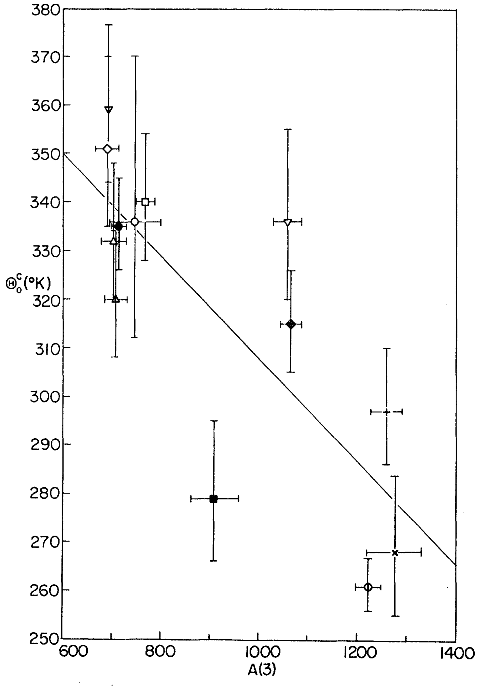

FIG. 4. Θ_0^c (°K) plotted against $A(3)$ (μcal units).

A recent density-of-states calculation, using the coherent-potential approximation, has been made for paramagnetic Cu-Ni alloys by Stocks, Williams, and Faulkner.[24] The results are consistent with x-ray photoemission spectroscopy experiments[25] and other work and show that separate undisplaced copper and nickel *d* bands exist. The calculated value[24] for the electronic specific-heat coefficient is (in the paramagnetic region) lower by 20–30% than the calorimetric values and the observation discussed in the previous paragraph would serve to increase this discrepancy. Even so, the difference is of the magnitude commonly observed for electron-phonon enhancement effects although other contributions of a magnetic nature may also occur.[8]

The dependence of observed Debye temperature on the magniutde of the cluster term [$A(3)$] is less certain (Fig. 4) but there does appear to be a decrease (corresponding to an increased lattice specific heat) with increased clustering. The line on Fig. 4 is a least-squares fit giving an intercept of 414 °K for no clustering. For isolated clusters of atoms the specific heat depends on the size of the cluster[26] (surface effects and a low-frequency cutoff of the phonon spectrum owing to the small size of the cluster) and it is possible that similar effects might occur in a clustered alloy. Room-temperature elastic constants of Cu-Ni alloys (of unknown cluster content) vary roughly linearly with composition[27] and, with some assumptions, it has been shown that Θ_0^c probably varies in the same way.[12] If this is so, decomposition of the alloy into the component parts would not affect the observed Θ_c^0 (Fig. 4). The Θ_0^c value (414 °K) for no clustering from Fig. 4 (on the assumption of a linear variation of Θ_0^c with the number of clusters) is higher than the calculated value (395 °K) from the elastic constants.[12] It is, of course, unlikely that the elastic data refer to an unclustered alloy which, following the preceding discussion, would be expected to have a higher value of Θ_0^c.

Dixon, Hoare, and Holden[11] measured a Cu–43-at.% Ni alloy in a chill cast, homogenized (furnace cooled), and quenched (from 1150 °C) condition. The variation in $A(3)$ and $A(4)$ observed for the homogenized and quenched conditions are similar to those reported in the present work. For the chill-cast condition the $A(3)$ is still over 50% of the $A(3)$ observed in the homogenized condition, but the $A(4)$ has increased considerably (18% from that observed in the homogenized condition) and perhaps lends some support to the high value obtained by extrapolation in Fig. 3. The only conclusion drawn from this earlier work[11] was that "no real change in the variation of specific heat with temperature is revealed after various annealing procedures," i.e., that clustering could not be prevented. This agrees with the findings of the present work which have also shown that the same conclusion applies to a much wider range of quenching temperatures.

The above discussion was on the assumption that the correct relation had been used to fit the specific heat. Falge and Walcott[12] have recently measured the specific heat of some Cu-Ni and Cu-Ni-Fe alloys in the range 0.43–6.2 °K or higher. They have fitted their results with an Einstein function and with a complicated Schottky function and state that in almost every case the standard deviation is markedly worse with an Einstein function than with a Schottky function. Unfortunately, they do not give the standard deviations and it appears from their discussion that the Schottky-function explanation is not without its difficulties. They also suggest that for some alloys the anomalous specific heat might be associated with a smeared cooperative transition corresponding to the Curie point. Their fitted Schottky curve for Cu–40-at.% Ni shows that the anomalous term reaches a maximum at about 1.5 °K and has fallen by an amount corresponding to about 2% of the total specific heat by 3 °K. If their interpretation of results is correct then the fitted equation used in the present work would require the terms $A(4)$ and $A(5)$ (electronic and lattice specific heat) to compensate for the Thirring expansion fitted to the cluster term. This might then account for the observed variation of electronic and lattice terms with the magnitude of the cluster term (Figs. 3 and 4). The variation of the sum of the electronic and lattice terms at 3 °K between the minimum and maximum values of the cluster term $[A(3)]$ is about 2% of the total specific heat which might be consistent with the Schottky function fit[12] assuming that the shape of the anomaly was independent of the number of clusters present. Using the linear extrapolation discussed above, the sum of the electronic and lattice terms changes by about 10% of the total specific heat on going from the greatest cluster value $[A(3)]$ observed to a zero cluster term. This change is surprisingly large compared with the 2% mentioned above but the changes in the total specific heat appear reasonable. Thus it cannot be argued that the present results are in favor of the Schottky-function fit of Ref. 12. Since they extend to only just beyond the maximum of the proposed Schottky function[12] they cannot be used to decide between the two methods of fitting. Whichever fit is taken as correct the general conclusions regarding the effect of quenching temperature on clustering will be unaltered. The observed variations of electronic and lattice terms as a function of the cluster term $A(3)$ might be spurious if the Schottky-function fit is correct. On the other hand, if the assumed linear variation is correct, the extrapolation to zero clustering should give the correct parameters for an unclustered alloy.

V. CONCLUSIONS

The specific heat of a Cu–40-at.% Ni alloy depends on heat treatment, the magnitude of the "cluster" term varying by a factor of roughly 2. It appears impossible to produce an unclustered alloy with the quenching technique and sample mass (50 g) used.

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Modified Lattice-Statics Approach to Point-Defect Calculations*

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A modified lattice-statics formalism is developed which allows anharmonic forces to be applied in determining the displacements of host atoms close to a point defect in a cubic lattice. The method is applied to determine the atomic relaxations in the vicinity of an octahedral carbon interstitial in α-iron and a single vacancy in α-iron. The displacements obtained for first and second neighbors to the vacancy are extremely close to those obtained by the semidiscrete method. The nearest neighbor to the carbon interstitial is displaced by an amount midway between the corresponding lattice-statics and semidiscrete values. The relaxation energy for the carbon interstitial is found to be −1.71 eV.

I. INTRODUCTION

The initial step in determining formation and migration energies associated with point defects in metals is the determination of the equilibrium configuration of host-lattice atoms in the vicinity of the defect. Once the relaxation of the host atoms is known, the energy changes arising from the expansion or contraction of interatomic bonds can be determined, given a suitable interatomic potential or a set of interatomic force constants.

At the present time, there are two basic approaches to the calculation of displacements of atoms in the presence of a point defect. The most widely used technique is one which will be referred to as the semidiscrete approach, in which the host atoms in a region of the lattice surrounding the defect are treated as discrete particles and the atoms in the remainder of the crystal are either held fixed at their perfect lattice positions or assumed to form an elastic continuum (usually isotropic). The configuration of atoms in the discrete region is then