PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Effect of Order on Residual Resistivity of Cu-Au Alloys above the Critical Temperature*

K. P. WANG AND H. AMAR

Department of Physics, Temple University, Philadelphia, Pennsylvania 19122

(Received 13 June 1969; revised manuscript received 22 September 1969)

We develop a pseudopotential theory of the residual resistivity of binary alloys as a function of short-range order. We apply our formulation to copper-gold alloys and compare our results with experimental data and with related theoretical studies.

I. INTRODUCTION

IN this paper we investigate the temperature dependence of the resistivity ρ ofa lloys above T_c, the critical temperature for long-range order. It has been experimentally observed that the differential coefficient $d\rho/dT$ may be positive or negative according to the alloys.[1,2] Relatively little work has been done towards the understanding of this general behavior. Perhaps the only significant work in this area is that of Gibson[3] who utilized both the Mott method in calculating the scattering matrix elements and the short-range-order parameters measured by Cowley.[4] The reliability of the latter parameters has been questioned by Moss[5] who repeated their measurement. The success of the pseudopotential method as used by Giaever[6,7] in the study of long-range-order dependence of the resistivity of alloys, suggests its applicability to the study of resistivity of alloys at high temperature. In view of this we have reexamined the whole problem, utilizing the more reliably measured short-range order (SRO) parameters, calculating the scattering matrix elements by the pseudopotential method,[7] and applying our results to the gold-copper alloys.

The resistivity of a metallic material is given by the general formula[7]

$$\rho=\frac{\Omega k_F m}{2\pi\hbar^3}\int_{\mathrm{FS}}|\langle k+q|W|k\rangle|^2(1-\cos\theta)\sin\theta d\theta\,,\qquad(1)$$

where $\langle k+q|W|k\rangle$ is the matrix element of the crystal potential between two Bloch states, k_F is the Fermi momentum, and θ is the angle between the initial Bloch state $|k\rangle$ and the final Bloch state $|k+q\rangle$. The integral is over the Fermi surface.

Introducing the new variable $x=q/k_F$, Eq. (1) can be transformed into the following equation[7]:

$$\rho=CN\int_0^2 |\langle k+q|W|k\rangle|^2 x^3dx\,,\qquad(2)$$

where N is the number of ions in the crystal, C is a constant which depends on the atomic volume per ion, Ω_0, and the Fermi energy E_F is given by

$$C=3\pi m\Omega_0/8\hbar e^2E_F\,.\qquad(3)$$

According to the pseudopotential theory, if W is taken as the pseudopotential, then $|k\rangle$ and $|k+q\rangle$ may be taken as plane waves, and the whole matrix element can be reduced in terms of the structure and form factors. The form factor has been tabulated for a large number of elements.

In Sec. II we give treatment of the resistivity of an n-component alloy and in Sec. III we specialize to binary alloys introducing the Cowley SRO parameters. In Sec. IV we apply our results to the alloys $\mathrm{Cu_3Au}$, CuAu, and $\mathrm{CuAu_3}$.

II. RESISTIVITY OF AN n-COMPONENT ALLOY

Consider a disordered n-component alloy with a total of N atoms of which $N_1, N_2, \ldots, N_n$ are of types 1, 2, ..., and n, respectively. Assume that these atoms are placed on a rigid Bravais lattice consisting of N sites. Further, postulate that the (pseudo) potential of the system can be written as a sum of the screened ionic pseudopotentials of types 1, 2, ..., and n, i.e.,

$$W(\mathbf{r})=\sum_i\sum_{\lambda=1}^{n}\sigma_i^\lambda w_\lambda(\mathbf{r}-\mathbf{r}_i)\,,\qquad(4)$$

where the occupation operators[8] σ_i^λ are defined as follows:

$$\sigma_i^\lambda=1,\quad\text{if the } i\text{th lattice site is occupied by an atom of type }\lambda$$
$$=0,\quad\text{otherwise}$$

and w_λ is the screened ionic pseudopotential of type λ. The matrix element $\langle k+q|W(\mathbf{r})|k\rangle$ between two plane-wave states $|k+q\rangle$ and $|k\rangle$ can thus be written as

$$\langle k+q|W(\mathbf{r})|k\rangle=\sum_i\frac{e^{-i\mathbf{q}\cdot\mathbf{r}_i}}{N}\sum_\lambda\sigma_i^\lambda\langle k+q|w_\lambda|k\rangle\,,\qquad(5)$$

---

* Supported by the U. S. Atomic Energy Commission.

[1] S. Radelaar, Phys. Chem. Solids **27**, 1375 (1966); R. Geary and S. Siegal, Phys. Rev. **65**, 347 (1944); J. B. Newkirk, R. Smolnchowski, A. H. Geisler, and D. L. Martin, J. Appl. Phys. **22**, 290 (1951); N. Thompson, Proc. Phys. Soc. (London) **52**, 217 (1940).

[2] A. Damask, J. Phys. Chem. Solids **1**, 23 (1956); P. Wright and K. F. Goddard, Proc. Phys. Soc. (London) **71**, 507 (1958); A. Damask, J. Phys. Chem. Solids **4**, 117 (1958); A. Damask, J. Appl. Phys. **27**, 610 (1956).

[3] J. B. Gibson, Phys. Chem. Solids **1**, 27 (1956).

[4] J. M. Cowley, J. Appl. Phys. **21**, 24 (1950); J. M. Cowley, Phys. Rev. **120**, 1648 (1960).

[5] S. C. Moss, J. Appl. Phys. **35**, 3547 (1964).

[6] I. Giaever, Ph.D. Thesis, Rensselaer Polytechnic Institute, 1964 (unpublished).

[7] W. A. Harrison, *Pseudopotentials in the Theory of Metal* (W. A. Benjamin, Inc., New York, 1966).

[8] R. A. Tahir-Kheli, Phys. Rev. **196**, 517 (1969).

where

$$\langle k+q|w_\lambda|k\rangle=\Omega_0^{-1}\int e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}w_\lambda(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}. \tag{6}$$

Let us introduce an "average lattice" and $(n-1)$ "difference lattices" through the following matrix elements:

$$\langle k+q|\bar{W}(\mathbf{r})|k\rangle\equiv\sum_i\langle\sigma_i^\lambda\rangle\langle k+q|w_\lambda|k\rangle \tag{7}$$

and

$$\langle k+q|\Delta w_{1\lambda}|k\rangle\equiv\langle k+q|w_1|k\rangle-\langle k+q|w_\lambda|k\rangle, \tag{8}$$

where $\langle\sigma_i^\lambda\rangle=\sum_i\sigma_i^\lambda/N=N_\lambda/N$. From Eqs. (7) and (8), we have, e.g.,

$$\langle k+q|w_1|k\rangle$$

$$=\langle k+q|\bar{W}(\mathbf{r})|k\rangle+\sum_{\lambda\neq1}\langle\sigma_i^\lambda\rangle\langle k+q|\Delta w_{1\lambda}|k\rangle \tag{9}$$

and

$$\langle k+q|w_\lambda|k\rangle=\langle k+q|\bar{W}(\mathbf{r})|k\rangle+\sum_{\lambda\neq1}\langle\sigma_i^\lambda\rangle\langle k+q|\Delta w_{1\lambda}|k\rangle$$

$$-\langle k+q|\Delta w_{1\lambda}|k\rangle\quad\text{for }\lambda\neq1. \tag{10}$$

Substituting (9) and (10) into (5), we have

$$\langle k+q|W(\mathbf{r})|k\rangle=\sum_i\frac{e^{-i\mathbf{q}\cdot\mathbf{r}_i}}{N}\langle k+q|\bar{W}|k\rangle$$

$$+\sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i}\sum_{\lambda\neq1}\{\langle\sigma_i^\lambda\rangle-\sigma_i^\lambda\}\langle k+q|\Delta w_{1\lambda}|k\rangle. \tag{11}$$

If $q=K_n$, one of the reciprocal lattice vectors of the average lattice, the terms in the second sum can be easily seen to be zero and we have

$$\langle k+q|W(\mathbf{r})|k\rangle=\sum_i\frac{e^{-i\mathbf{K}_n\cdot\mathbf{r}_i}}{N}\langle k+q|\bar{W}|k\rangle$$

$$=\sum_\lambda\frac{N_\lambda}{N}\langle k+q|w_\lambda|k\rangle. \tag{12}$$

In this case the matrix element is independent of the arrangement of the atoms. Therefore, it is of no interest for our purpose.

If $q\neq K_n$, then the first term of Eq. (11) vanishes. We have

$$\langle k+q|W(\mathbf{r})|k\rangle$$

$$=\sum_i\frac{e^{-i\mathbf{q}\cdot\mathbf{r}_i}}{N}\sum_{\lambda\neq1}(\langle\sigma_i^\lambda\rangle-\sigma_i^\lambda)\langle k+q|\Delta w_{1\lambda}|k\rangle. \tag{13}$$

The square of the matrix element $\langle k+q|W(\mathbf{r})|k\rangle$, after simple manipulations, can be written as

$$|\langle k+q|W(\mathbf{r})|k\rangle|^2$$

$$=\sum_l\frac{e^{-i\mathbf{q}\cdot\mathbf{r}_l}}{N}\sum_{\lambda,\lambda'\neq1}\langle(\langle\sigma_i^\lambda\rangle-\sigma_i^\lambda)(\langle\sigma_{i-l}^{\lambda'}\rangle-\sigma_{i-l}^{\lambda'})\rangle$$

$$\times\langle k+q|\Delta w_{1\lambda}|k\rangle\langle k+q|\Delta w_{1\lambda'}|k\rangle^*, \tag{14}$$

where $\langle(\langle\sigma_i^\lambda\rangle-\sigma_i^\lambda)(\langle\sigma_{i-l}^{\lambda'}\rangle-\sigma_{i-l}^{\lambda'})\rangle$ are the correlation functions which are functions of the temperature and of the interatomic potentials.[8,9] Their (inverse lattice) Fourier transforms are either related to the scattered diffuse x ray or to neutron intensities. They are defined as

$$\langle(\langle\sigma_i^\lambda\rangle-\sigma_i^\lambda)(\langle\sigma_{i-l}^{\lambda'}\rangle-\sigma_{i-l}^{\lambda'})\rangle$$

$$\equiv\sum_i\frac{[\langle\sigma_i^\lambda\rangle-\sigma_i^\lambda][\langle\sigma_{i-l}^{\lambda'}\rangle-\sigma_{i-l}^{\lambda'}]}{N}. \tag{15}$$

It is interesting to note that each term of Eq. (14) has been factorized into a structural part

$$\sum_l\frac{e^{-i\mathbf{q}\cdot\mathbf{r}_l}}{N}\langle(\langle\sigma_i^\lambda\rangle-\sigma_i^\lambda)(\langle\sigma_{i-l}^{\lambda'}\rangle-\sigma_{i-l}^{\lambda'})\rangle$$

which depends on the arrangement of the ions present in the lattice, and an "atomic part,"

$$\langle k+q|\Delta w_{1\lambda}|k\rangle\langle k+q|\Delta w_{1\lambda'}|k\rangle$$

which is independent of the crystal structure and is directly related to the tabulated form factors.[7]

By substituting (14) into (2), we succeed in expressing the resistivity in terms of correlation functions and form factors, i.e.,

$$\rho=CN\int_0^2\sum_l\frac{e^{-i\mathbf{q}\cdot\mathbf{r}_l}}{N}\sum_{\lambda,\lambda'\neq1}\langle(\langle\sigma_i^\lambda\rangle-\sigma_i^\lambda)(\langle\sigma_{i-l}^{\lambda'}\rangle-\sigma_{i-l}^{\lambda'})\rangle$$

$$\times\langle k+q|\Delta w_{1\lambda}|k\rangle\langle k+q|\Delta w_{1\lambda'}|k\rangle^*x^3dx. \tag{16}$$

The complicated correlation functions (15) are mutually related and difficult to measure for alloys of three or more components. Their presence in (16) limits its applicability to binary alloys only.

III. RESISTIVITY OF BINARY ALLOYS

In this case the λ,λ' summation in (16) reduces to one term only, corresponding to $\lambda=\lambda'=2$,

$$\rho=CN\int_0^2\sum_l\frac{e^{-i\mathbf{q}\cdot\mathbf{r}_l}}{N}\langle(\langle\sigma_i^2\rangle-\sigma_i^2)(\langle\sigma_{i-l}^2\rangle-\sigma_{i-l}^2)\rangle$$

$$\times|\langle k+q|\Delta w_{12}|k\rangle|^2x^3dx. \tag{17}$$

It is easy to show that the correlation function $\langle(\langle\sigma_i^2\rangle-\sigma_i^2)(\langle\sigma_{i-l}^2\rangle-\sigma_{i-l}^2)\rangle$ or $\langle\sigma_i\sigma_{i-l}\rangle$, where $\sigma_i\equiv\langle\sigma_i^2\rangle-\sigma_i^2$, is related to the Cowley short-range-order parameters[4] by the following equation:

$$\langle\sigma_i\sigma_{i-l}\rangle=m_1m_2\alpha_l, \tag{18}$$

where m_λ is the composition of the λ-type atom. Sub-

---

[9] P. C. Clapp and S. C. Moss, Phys. Rev. **142**, 418 (1966); **171**, 754 (1968); S. C. Moss and P. C. Clapp, *ibid.* **171**, 764 (1968).

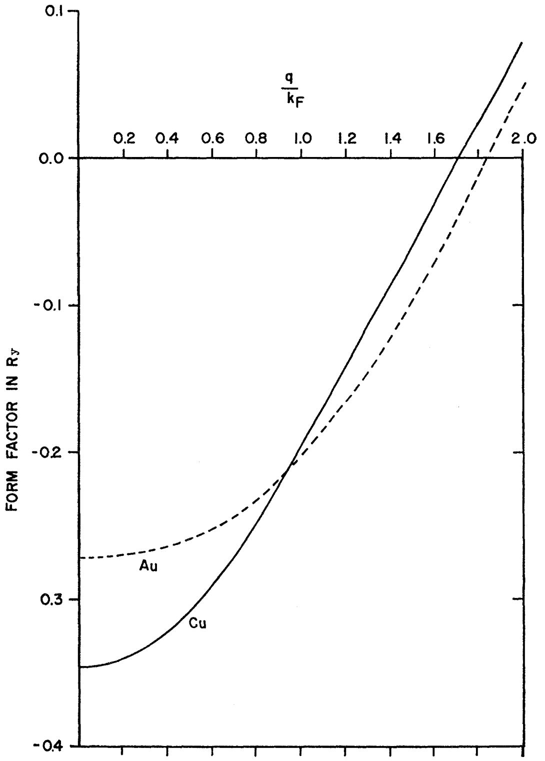

FIG. 1. Form factors of Cu and Au calculated by Animalu as a function of q/k_F based on the method due to Heine, Abarenkov, and Animalu.

stituting (18) into (17) we have

$$\rho=Cm_1m_2\int_0^2 \sum_l e^{-i\mathbf{q}\cdot\mathbf{r}_l}\alpha_l|\langle k+q|\Delta w_{12}|k\rangle|^2x^3dx. \quad (19)$$

For the purely random case,

$$\alpha_0=1,$$
$$\alpha_{l\neq 0}=\frac{-1}{N-1}\simeq 0 \quad \text{for large } N. \quad (20)$$

Therefore, we have

$$\rho=Cm_Am_B\int_0^2 |\langle k+q|\Delta w_{12}|k\rangle|^2x^3dx.$$

This gives the familiar parabolic dependence of the resistivity upon concentration for a binary alloy as, for example, obtained by Harrison.[7]

We introduce the Cowley scalar short-range-order parameter which can be measured either via the x-ray or neutron diffraction experiment, i.e.,[4]

$$\alpha_i=C_i^{-1}\textstyle\sum_l \alpha_l, \quad (21)$$

where the summation is over the vectors belongs to ith shell and C_i is the coordination number for the ith shell. In terms of the Cowley scalar order parameter, Eq. (19) can be written as

$$\rho=Cm_1m_2\int_0^2 \sum_{i,\mathbf{n}_i} e^{-i\mathbf{q}\cdot\mathbf{n}_i}\alpha_i|\langle k+q|\Delta w_{12}|k\rangle|^2x^3dx, \quad (22)$$

where the vectors $\mathbf{n}_i$ locate the atoms in the ith shell.

Following Gibson,[3] Eq. (22) can be further simplified as follows. The exponential factor appearing in Eq. (22) can be expanded into a series involving the spherical Bessel functions and Legendre polynomials, i.e.,

$$\sum_{i,\mathbf{n}_i}\alpha_i\sum_l (2l+1)(-i)^lj_l(n_iq)P_l(\cos\theta_{\mathbf{n}_i}). \quad (23)$$

In a metallic structure there will be in general several neighbors at a given distance and they will be symmetrically distributed. Thus, a sum over the angle might reasonably be approximated by an integral over the angle, i.e.,

$$\sim\sum_i\sum_l (2l+1)(-i)^lj_l(n_iq)\alpha_i\frac{C_i}{4\pi}\int P_l(\cos\theta_{\mathbf{n}_i})$$
$$\times 2\pi\sin\theta_{\mathbf{n}_i}d\theta_{\mathbf{n}_i}=\sum_i \alpha_iC_ij_0(n_iq). \quad (24)$$

Therefore, with this approximation,

$$\rho=Cm_1m_2\int_0^2 |x\langle k+q|\Delta w_{12}|k\rangle|^2\sum_i \alpha_iC_ij_0(n_iq)xdx. \quad (25)$$

Despite its appearance, Eq. (25) differs appreciably from Gibson's Eq. (16) in that the Bloch states have been replaced by plane waves and the atomic potentials by appropriate pseudopotentials. It can be readily used to calculate the contribution of short-range order to the resistivity above the critical temperature T_c for binary alloys. We shall apply it to the Cu-Au systems.

IV. APPLICATION TO Cu-Au ALLOYS

Copper and gold form a continuous solid solution at all compositions with ordered structures occurring (at sufficiently low temperature) at the stoichiometric compositions Cu_3Au, CuAu, and $CuAu_3$, all of which have been extensively studied. At low temperature, Cu_3Au has perfect long-range order with the Cu atoms at the face centers and the Au atoms at the cube corners. The long-range order decreases with increasing temperature and it drops sharply to zero at the critical temperature $T_c=390$°C.[4,5] The CuAu alloy has three phases.[10] Below 380°C, CuAu I has a tetragonal face-centered structure with the c axis normal to the alternating atomic layers of Cu and Au ($c/a=0.93$). In the temperaperature range 380–410°C, we have CuAu II. It is characterized by the existence of a long period superlattice. The unit cell of CuAu II is orthorhombic. Above 410°C, CuAu, known as CuAuD, is statistically face-centered cubic and has only a short-range order. The

---

[10] B. W. Roberts, Acta Met. 2, 597 (1954).

phase transformation from CuAu I to CuAu II and that from CuAu II to CuAuD are all first-order transformations.[11] Like Cu_3Au, the structure of $CuAu_3$ is also face-centered cubic but with Cu and Au interchanged in position. $CuAu_3$ undergoes a first-order phase transformation at the critical temperature approximately equal to 200°C.[12]

$\rho(T)$ was calculated at two temperatures for each of three alloys:

$$\begin{aligned} &Cu_3Au && \text{at} && T=405°\text{C and } T=460°\text{C}\,,\\ &CuAuD && \text{at} && T=245°\text{C and } T=525°\text{C}\,,\\ &CuAu_3 && \text{at} && T=250°\text{C and } T=320°\text{C}\,. \end{aligned}$$

Before presenting the results we shall outline the calculational method. This is essentially based on formula (25). The integrand in Eq. (25) consists of two parts; one is structural in nature,

$$S \equiv x \sum_i \alpha_i C_i j_0(n_i q)\,, \tag{26}$$

which involves the short-range-order parameters and varies with temperature; the other is the atomic part, $|x\langle k+q|\Delta W_{12}|k\rangle|^2$, which involves the form factors of Cu and Au. In the present calculation, two different form factors for Cu and Au were used. One is due to Animalu[13] based on the method of Heine, Abarenkov, and Animalu.[14–17] The other is due to Giaever[6] based on the point-ion approximation.[7] The Animalu form factors for Cu and Au were plotted in Fig. 1 as a function of q/k_F. Using the form factors of Giaever and those of Animalu, we calculated the difference $\langle k+q|W_{Cu}|k\rangle - \langle k+q|W_{Au}|k\rangle$. Figure 2 illustrates the comparison between the two results. The structure factors for each alloy were calculated using the measurements due to Moss,[5] Roberts,[10] and Batterman.[12] The summation is cut off at either the tenth or eighth shell according to the measurements. The calculation of structure factors and the integration appearing in Eq. (25) were performed on the Temple CDC 6400 computer with a mesh equal to 0.01.

The results of our calculation are as follows:

(a) Cu_3Au: The resistivity for this alloy was calculated at $T=405°$C and $T=460°$C. The short-range-order parameters measured by Moss[5] were used in calculating the structure factor S. The results for these two temperatures are plotted as functions of q/k_F and are shown in Fig. 3. The main peaks occur approximately at $q/k_F=1.33$ and 1.45, respectively. As the temperature increases the main peak drops slightly and the shoulder (approximately around $q/k_F=1.86$ at $T=405°$C) disappears. Using these structure factors along with the form factors plotted in Fig. 1, we found that as the temperature goes from 405 to 460°C, the residual resistivity drops from 2.773 to 2.667 μΩ cm (we used $a=7.0824$ a.u. for the lattice constant), approximately a 3.8% decrease. Damask[2] observed a decrease of 0.4% (measured at 77°K), in qualitative agreement with our calculation.

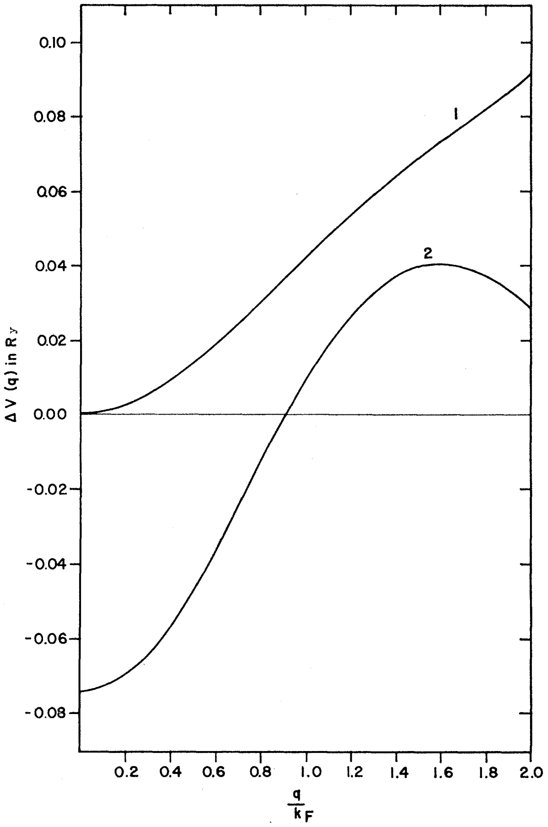

FIG. 2. Comparison of $\langle k|w_{Cu}|k+q\rangle - \langle k|W_{Au}|k+q\rangle$ calculated using (1) the method of point-ion approximation, and (2) the method of Heine, Abarenkov, and Animalu.

We would like to comment here about the comparison of our calculation with experimental results. These comments apply also to the cases of CuAu and $CuAu_3$. (1) As our theory does not include phonons, a comparison between theory and experiment is meaningful only when the effect on ρ of phonons is negligible as compared with that of SRO. (2) While our calculation is based on at-temperature SRO, the measurement of residual resistivity is made on quenched samples held at 77 or 4°K. It has been reported that quenching can give strange results which are not necessarily related to SRO at $t>t_c$. One, for example, is the presence of excess quenched-in-lattice vacancy concentration.[18] (3) Changes in static displacement have an effect on ρ which might be comparable to the effect produced by changes in SRO. This effect (due to changes in static displacement) is very difficult to assess from the experimental results. In view

---

[11] M. Tachiki and K. Teramoto, J. Phys. Chem. Solids **27**, 335 (1966).

[12] B. W. Batterman, J. Appl. Phys. **28**, 556 (1957).

[13] A. O. E. Animalu (private communication).

[14] I. V. Abarenkov and V. Heine, Phil. Mag. **12**, 529 (1965).

[15] V. Heine and I. V. Abarenkov, Phil. Mag. **9**, 451 (1964).

[16] A. O. E. Animalu, Phil. Mag. **11**, 379 (1965).

[17] A. O. E. Animalu, and V. Heine, Phil. Mag. **12**, 1249 (1965).

[18] S. Benci, G. Gasparrini, and E. Germagnoli, Nuovo Cimento **31**, 1165 (1964).

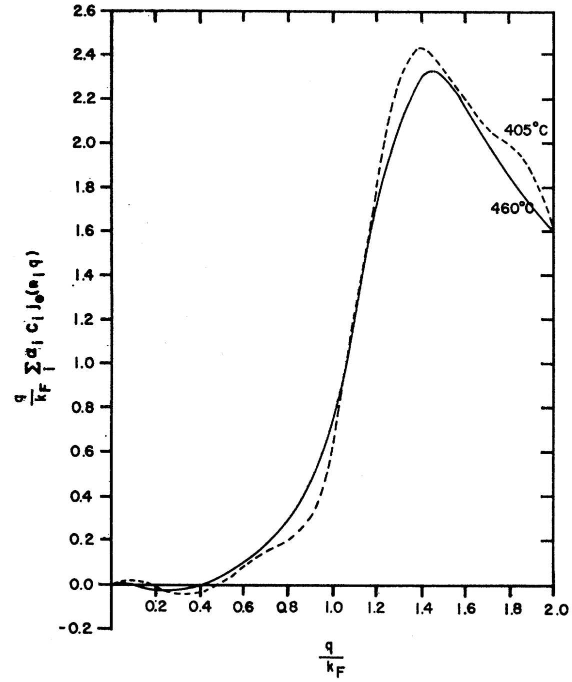

FIG. 3. Structure factor S of Cu_3Au as a function of q/k_F at $T=405$ and $T=460$°C. The calculation is based on Moss's measurements.

of the above, the numerical comparison of our results with experimental data must be made cautiously.

Some years ago, Gibson[3] calculated the resistivity of Cu_3Au above the critical temperature as a function of the short-range order. In his work, the Mott approximation was used for calculating the scattering matrix elements and the short-range-order parameters measured by Cowley[4] were used to calculate the structure factor S. He found a decrease of about 1% as the temperature increases from 405 to 460°C. Using Animalu's form factors and the structure factors based on the Cowley measurements, we found a decrease in resistivity of about 0.9%. Both this calculation and that of Gibson agree very well with the experimental value 0.4% reported by Damask. However, we believe that these agreements are fortuitous since the measurements due to Moss are definitely more reliable than those of Cowley. In Moss's measurements,[5] corrections were made for the temperature effect as well as the size effect. Thus, we believe that a 3.8% decrease in resistivity is probably closer to reality. The structure factors based on Cowley's measurements were calculated and plotted in Fig. 4 for the purpose of comparison.

We have also made a similar calculation using the form factors based on the point ion approximation as Giaever[6] did. The results show that as the temperature increases from 406 to 460°C, the resistivity decreases from 12.26 to 11.26 $\mu\Omega$ cm, about a 4.1% decrease (we used the same lattice constant, $a=7.0824$ a.u.). These results give the correct trend. But, in view of the large value of residual resistivity due to short-range order alone, it is likely that the point-ion approximation is not the best suited for this kind of calculation.

(b) CuAu: The short-range order in CuAu was measured by Roberts[10] following the method used by Cowley on Cu_3Au. In this method, no corrections for the temperature diffuse scattering and the size effect are made. In view of these shortcomings, the results reported by Roberts are somewhat unreliable. Using Roberts's measurements, we have calculated the structure factors at $T=425$ and 525°C. They are shown in Fig. 5. There are two main peaks occurring at $q/k_F=1.33$ and 1.93, respectively. The height of these peaks decreases slightly as the temperature goes up. Using these structure factors, we found that the resistivity decreases from 3.499 to 3.440 $\mu\Omega$ cm, about a 1.7% decrease, as the temperature increases from 425 to 525°C (lattice constant = 3.86 Å, quenched from 600°C). Although much experimental work has been done on CuAu, we can find no suitable data for comparison with our calculation.

(c) $CuAu_3$: The resistivity behavior of $CuAu_3$, both below and above the critical temperature, resembles that of Cu_3Au. Wright and Goddard[19] observed a rise

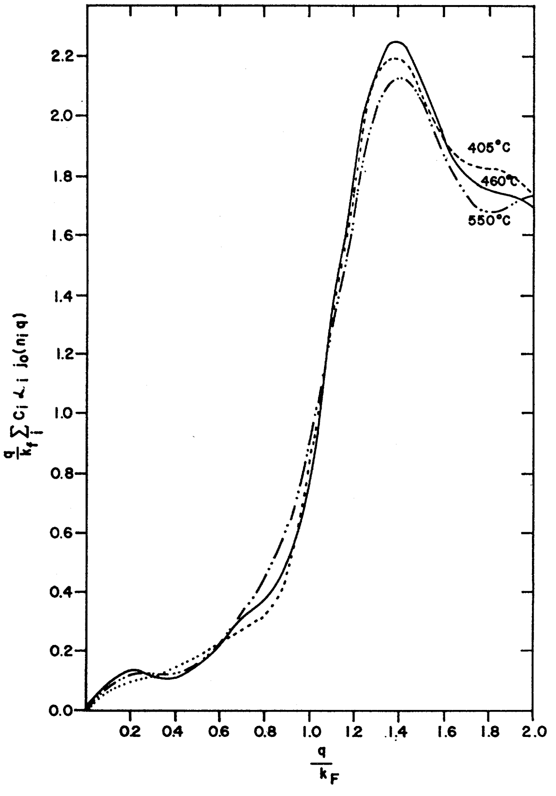

FIG. 4. Structure factor S of Cu_3Au as a function of q/k_F as $T=405$, 460, and 550°C. The calculation is based on Cowley's measurements.

---

[19] P. Wright and K. F. Goddard, Proc. Phys. Soc. (London) **71**, 507 (1958).

in the resistivity of $CuAu_3$ between 300 and 190°C as the critical temperature approached from high temperatures. Just as in Cu_3Au, they also observed a small maximum which occurs between 400 and 600°C. In view of the similarity between Cu_3Au and $CuAu_3$, one would expect the theoretical results to be similar for both alloys. However, for $CuAu_3$, our calculated results show that instead of a decrease in resistivity, a slight rise in resistivity is obtained, from 3.24 to 3.25 $\mu\Omega$ cm as the temperature goes up from $T=250$ to $T=320$°C. We speculate that this disagreement is mainly due to the inaccurate measurement of the short-range order reported by Batterman.[12] As pointed out by Batterman himself, the largest sources of error lie in the approximate nature of the temperature and size-effect corrections. The structure factors at $T=250$ and $T=320$°C are shown in Fig. 6. The reason for believing that $d\rho(T)/dT$ is positive in the stoichiometric alloys can be stated as follows: When the temperature is high an electron in the crystal feels a statistically periodic average potential. As the temperature decreases, the short-range order increases, i.e., the number of small domains of nearest-neighbor order increases. Thus the scattering potential becomes stronger and the resistivity increases. If the temperature further decreases, the number of small domains and also their size will increase. As the critical temperature is approached, the domains finally become stable and coalesce to give a coherent scheme of long-range order.

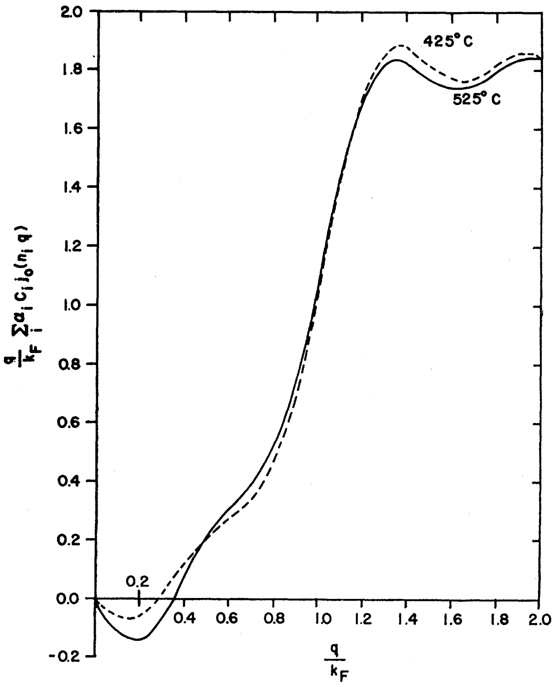

FIG. 5. Structure factor S of CuAuD as a function of q/k_F at $T=425$ and $T=525$°C. The calculation is based on Roberts's measurements.

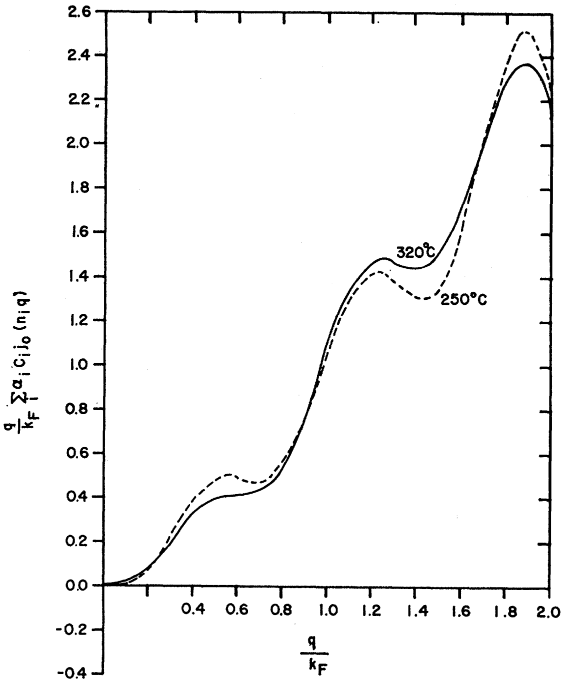

FIG. 6. Structure factor S of $CuAu_3$ as a function of q/k_F at $T=250$ and $T=320$°C. The calculation is based on Batterman's measurements.

Our calculations may be criticized on several grounds. First, the pseudopotentials theory of alloys assumes that the individual atomic pseudopotential is unaffected by alloying. Second, the validity of the proposed form factors for the noble metal, is still an open question. Moreover, one may question the use of first-order perturbation theory, as well as the fact that the convergence of series (26) is not well known. Despite these uncertainties, we feel that our calculations constitute a progress towards an understanding of the residual resistivity of Cu-Au alloys above the critical temperature. They are most promising in the case of Cu_3Au, where the short-range-order data are more reliable.

ACKNOWLEDGMENT

We are grateful to Dr. A. O. E. Animalu for sending us the form factors of noble metals.