Electron transport and neutron diffraction evidence for chemical short-range order in liquid Cu_6Ce

LETTER TO THE EDITOR

Electron transport and neutron diffraction evidence for chemical short-range order in liquid Cu_6Ce

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Abstract. We have measured the electronic resistivity and thermopower of liquid $Cu_{1-c}Ce_c$, $Cu_{1-c}La_c$, and $Ag_{1-c}Ce_c$ alloys for $c < 0.4$. In all of the alloys the resistivity is very similar, rising smoothly and steeply as c increases, but at all times remaining less than 200 $\mu\Omega$ cm. The thermopower is also featureless and metallic. However, the temperature coefficient, $\alpha = (1/\rho)d\rho/dt$, displays in the Cu alloys a minimum for Cu_6RE (RE = rare earth), which furthermore is negative for Cu_6Ce; a negative temperature coefficient is also seen for Ag_3Ce. We also present the results of an investigation of neutron diffraction scattering from liquid Cu_6Ce, and the results of a reverse Monte Carlo (RMC) analysis of the structure data, which shows evidence of ordering in the liquid, with characteristics similar to those of crystalline Cu_6Ce. We discuss several possible explanations for the negative temperature coefficient of both Ag and Cu alloys, and conclude that its origin lies in the presence of chemical short-range order.

The resistivities of liquid alloys of copper with rare earths (RE) were first studied by Güntherodt *et al* [1]. All of the alloys studied, including those containing La, Ce, Nd, and Pr, show remarkably similar behaviour up to 40 at.% RE. Furthermore, the highest resistivity of the alloys, occurring approximately at the equiatomic concentration, is still metallic as indicated by its magnitude. In addition, the temperature coefficient of the resistivity, $\alpha = (1/\rho)d\rho/dT$, was for all of the alloys at all of the concentrations determined to be small and positive. A simple description seemed in order, due to the apparent lack of effect on ρ or α of the additional f electrons contributed by the REs; weak-scattering Faber–Ziman theory seemed appropriate because the magnitude of the resistivity was far less than in divalent liquid Ba ($\rho = 338$ $\mu\Omega$ cm [2]), which was successfully modelled by the theory.

In later structure measurements by means of anomalous x-ray diffraction, Cu–Ce was determined by Waseda [3] to be unremarkable across a wide range of rare-earth concentrations; Waseda suggested that the alloy was most probably a simple random mixture of Ce and Cu atoms, on the basis of the apparent invariability with respect to Ce content of the peak positions in the partial structure factors. However, no structure measurements were made below 20 at.% Ce.

Additional recent interest in some RE alloys stems from the fact that they are heavy-fermion compounds. This is also true for Cu_6Ce. Sputter-deposited amorphous Cu_6Ce was discovered comparatively recently by Suzuki *et al* [4] to display at low temperatures the $-\log(T)$ dependence of the resistivity characteristic of heavy-fermion behaviour, and similar to the behaviour recorded previously for Cu_6Ce crystal [5]. The amorphous alloy

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shows a continued linear temperature dependence of ρ with negative α up to the highest temperature surveyed, about 300 K. The absence of thermopower data for liquid Cu–RE compounds, the availability of high-purity materials, and the unusual negative temperature coefficient (NTC) for the amorphous solid have prompted us to systematically study these liquid materials. We have for comparison measured the electronic transport properties of liquid Ag–Ce; we believe that these are the first electronic transport measurements on this liquid system. In addition, we have conducted a neutron diffraction study of liquid Cu_6Ce, and have also done a reverse Monte Carlo (RMC) analysis. The results of the transport measurements and the structure measurements are discussed separately below.

We obtained sample materials from AESAR/Johnson–Matthey: lot analyses of La and Ce yielded impurity levels of 60 and 200 ppm (by weight), respectively; Ag and Cu, from the same supplier, were of 99.99% and 99.999% purity. Samples were prepared and handled under an argon atmosphere in an evacuable glove box to avoid contamination. During measurements, our alloys were held in high-density Al_2O_3 tubes, and were stirred vigorously to ensure uniformity. The sample material separated easily from the wall of the post-experiment tube, and no reaction is thought to have occurred. (For a more detailed description of the sample containment, see Walhout *et al* [6].) The resistivity was measured using a standard four-probe technique, and the thermopower was measured against chromel counter-electrodes [7]; the uncertainty in the absolute thermopower of chromel is estimated to be $+0.2$ μV $^\circ$C^{-1}. The errors in the resistivity and the thermopower are calculated from a least-squares fit to all of the data, and in the majority of cases do not exceed 0.5 $\mu\Omega$ cm and 0.3 μV $^\circ$C^{-1}, respectively.
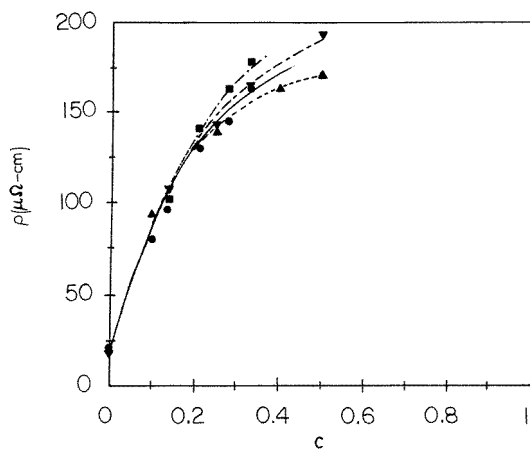
Figure 1. ρ as a function of the atomic fraction, c, of RE, for the liquid alloys Cu–Ce, Cu–La, Cu–Nd, and Ag–Ce. Present results: ● Cu–Ce; ■: Cu–La; and ▼: Ag–Ce. From reference [8]: ▲: Cu–Nd. In all cases, the error bars are encompassed by the symbols.

Our results for the resistivity of liquid Cu–Ce are shown in figure 1, along with our data for Cu–La and Ag–Ce, and Cu–Nd data given by Güntherodt and Zimmermann [8]. All of the data points shown are from a linear fit to all of the data, evaluated at 950 $^\circ$C, except for the Ag alloys, which were evaluated at 1050 $^\circ$C. In all cases, the resistivity rises smoothly from that of pure Cu(Ag) as the rare-earth content is increased. The resistivities of the different alloys are remarkably similar up to 35 at.% RE; none of the alloys show any features in the resistivity, even at Cu_6RE or Cu_2RE, or at Ag_3Ce, which are the

concentrations of congruently melting crystalline compounds, and correspond to peaks in the melting curve. Even near the equiatomic concentration and the highest resistivity in the alloys, all of the materials have values of the resistivity which are well within the bounds of metallic conduction.
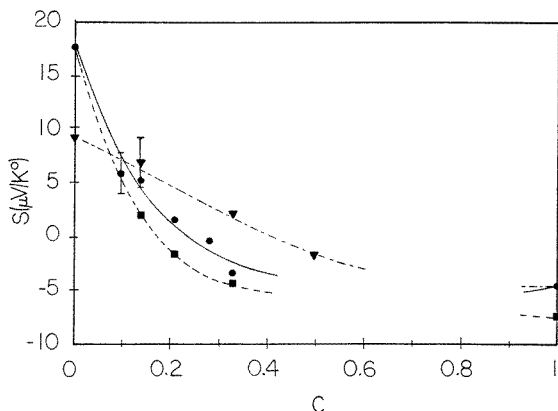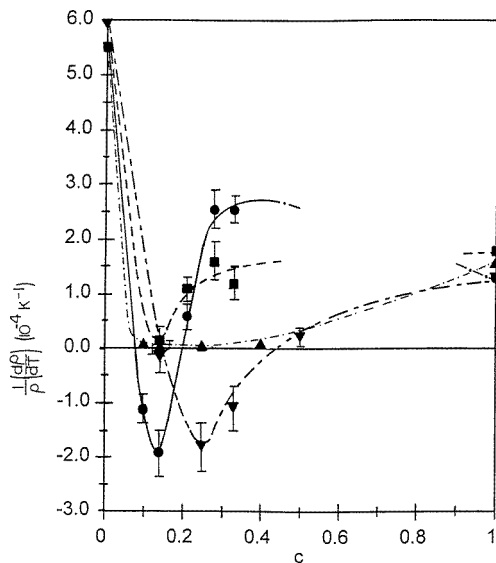

Figure 2. S as a function of the atomic fraction, c, of RE, for the liquid alloys Cu–Ce, Cu–La, and Ag–Ce. Present results: ●: Cu–Ce; ■: Cu–La; and ▼: Ag–Ce. Unless shown, the error bars are to be considered smaller than the extent of the symbols.

Figure 2 displays the concentration dependence of the thermopower; in all cases, dS/dc is quite steep from pure Cu(Ag) to $\sim$30 at.% rare earth; again, S is featureless and smooth, and at all of the concentrations examined has a value which is decidedly metallic and between the values of S for the pure constituents.

Figure 3 shows the concentration dependence of the temperature coefficient of the resistivity, α. For Cu–Nd, α is quite small and positive over a wide range of RE concentration, but appears to have a very shallow minimum at Cu_6Nd. For both Cu_6Ce and Cu_6La, α is markedly depressed compared to the values for surrounding concentrations, and furthermore is negative for Cu_6Ce. It is highly unusual to see structure in α and not in the resistivity or thermopower; furthermore, to our knowledge, this is the lowest resistivity found in a liquid alloy—about 95 $\mu\Omega$ cm—associated with a NTC. Our value of $\alpha = -1.8 \times 10^{-4}$ °C^{-1} is comparable to that seen for divalent pure liquid elements like Sr and Zn, and for the divalent alloy SnCe. For Ag_3Ce, $\alpha = -1.6 \times 10^{-4}$ °C^{-1}, but, again, no features are seen in ρ or S.

For all of the materials studied, the minima in α correspond to peaks in the melting curve. The alloys Cu_6RE, for RE = La, Ce, Pr, and Nd, all possess the same crystal structure and melt congruently from an orthorhombic structure; Ag_3Ce melts from a hexagonal crystal structure. It is interesting that the minimum in α around stoichiometry is most pronounced for Cu_6Ce, which has the highest melting point among the Cu–RE compounds studied, and is least pronounced for Cu_6Nd, the compound with the lowest melting point. With this in mind, we have conducted a neutron diffraction study of liquid Cu_6Ce.

The neutron diffraction study was performed on the GLAD (Glass, Liquid, and Amorphous Diffractometer) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. Sample material of the purity noted earlier was prepared in an argon atmosphere, as above, and was initially melted and stirred in an alumina tube under argon, prior to being sealed under argon in a vanadium tube for the scattering experiment. The

Figure 3. $(1/\rho)\mathrm{d}\rho/\mathrm{d}t$ as a function of the atomic fraction, c, of RE, for the liquid alloys Cu–Ce, Cu–La, Cu–Nd, and Ag–Ce. Present results: ● Cu–Ce; ■: Cu–La; and ▼: Ag–Ce. From reference [8]: ▲: Cu–Nd. Data for pure liquid Ce, La, and Nd are from reference [15].

alloy sample was not at any time exposed to the atmosphere. The experiment was conducted at 1000 °C within a cylindrical vanadium furnace in a vacuum. Data for the empty tube, and for the furnace, were subtracted from the experimental spectra before analysis.
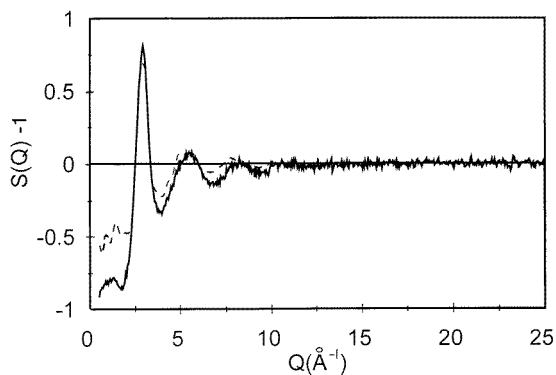
Figure 4. The experimental total structure factor, $S(Q) - 1$, for liquid Cu_6Ce (solid line), shown with the reversed Monte Carlo fit started from the crystalline configuration of 3500 atoms (dashed line).

The experimental structure factor, $S(Q) - 1$, is shown in figure 4. A significantly robust prepeak is seen at 1.6 $\mathrm{\mathring{A}}^{-1}$; for other alloys, a prepeak in the structure factor at a low Q-value has been interpreted [9] as evidence of CSRO.

Fourier transformation of the data up to $Q = 25$ $\mathrm{\mathring{A}}^{-1}$, using a Lorch window for truncation, leads to the pair correlation function $g(r)$. The total correlation function, $T(r) = rg(r)$, is shown in figure 5. The main peak in $T(r)$ is at 2.5 $\mathrm{\mathring{A}}$, and a shoulder is
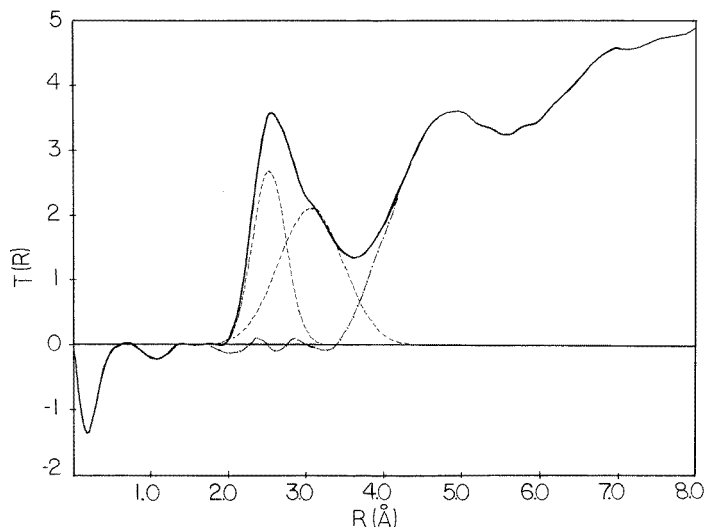
Figure 5. The total correlation function, $T(r) = rg(r)$; $g(r)$ is obtained by Fourier transformation of the experimental structure factor, $S(Q)$, for liquid Cu_6Ce. The dashed lines result from a Gaussian deconvolution of $T(r)$.

seen on the high-r side at 3.05 Å. Because of the relative concentrations of Cu and Ce, and because the scattering length of Cu is nearly twice that of Ce, the structure seen in $T(r)$ is most significantly composed of Cu–Cu correlations. The total structure factor may be calculated according to the following formula:

$$S(Q) = \sum_{ij} c_i c_j b_i b_j (S_{ij}(Q) - 1)$$

where c_i is the concentration of constituent i, b_i is the scattering length, and $S_{ij}(Q)$ is the partial structure factor. For our alloy, the weightings of the partials are as follows: Cu–Cu = 0.4375, Cu–Ce = 0.0916, and Ce–Ce = 0.0048.

The coordinations may be calculated from the areas of Gaussians fitted beneath the $T(r)$ curve. The Gaussian centred at 2.5 Å is certainly CuCu correlation exclusively; the other at 3 Å, however, is probably a combination of CuCu and CuCe coordinations, mostly CuCu. If we take the total area under both Gaussians as CuCu, we calculate a CuCu coordination of 10.7, which compares favourably with the average coordination of Cu to Cu in crystalline Cu_6Ce calculated out to 4 Å, about 9.3. However, CuCe distances of ~3–3.4 Å also exist in the crystal, and almost certainly comprise a portion of the second Gaussian. To continue this analysis, we have utilized RMC analysis to examine the structure factor further, and to shed light on the origin of the prepeak.

Two different initial configurations were selected for our simulations.

(1) A random arrangement of 1050 atoms of the stoichiometric concentration. The following minimum distances of approach were used: $r_{CuCu} = 2$ Å, $r_{CuCe} = 2.55$ Å, and $r_{CeCe} = 2.85$ Å, very similar to the first-peak positions of liquid $Cu_{0.75}Ce_{0.25}$, according to the anomalous x-ray diffraction results of Waseda [3].

(2) A crystalline configuration of Cu_6Ce [10], with 3500 atoms, and with the minimum distances of approach the same as above. The program fitted the calculated $S(Q)$ to the experimental structure factor data; the results are shown in figure 4.

The quality of the fitting parameter, χ^2, of the simulation started from the initial crystalline configuration, and of the simulation started from a random initial arrangement ultimately converged to within 2% of one another; both simulations were successful at reproducing the prepeak.
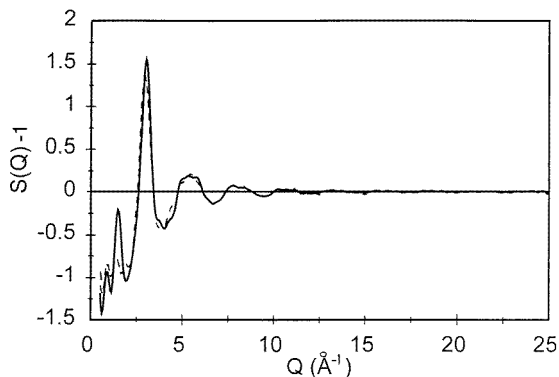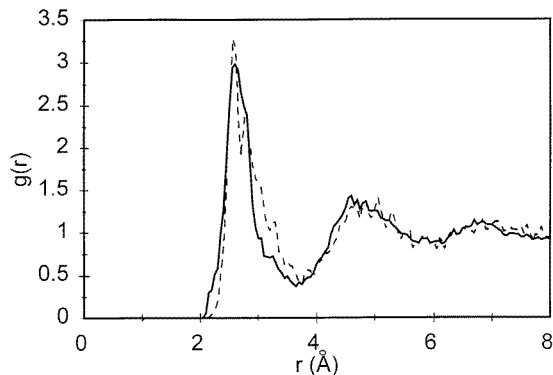

Figure 6. The RMC partial structure factor, $S_{CuCu}(Q) - 1$, for liquid Cu_6Ce: dashed line: results from a simulation starting from a random initial configuration; solid line: results from a simulation starting from the crystalline initial configuration.

The main peak in $S(Q)$ is very well reproduced in height, width, and position for both starting configurations, but for the second and following peaks the RMC fits were less effective. The baseline against which the height of the prepeak may be measured appears to have been set rather too high by the simulation. However, for both simulations, the height of the peak in $S(Q)$ with regard to this baseline is in good agreement with the height of the experimental peak, but it is only as pronounced as the experimental prepeak in the simulation starting from the crystalline arrangement. The prepeak is found in both cases in the CuCu partial structure factor; and is centred at 1.6 $\mathring{A}^{-1}$ (figure 6). At the same momentum transfer, there is a deep minimum in the CeCu partial, which, in spite of its significantly lower weighting in the total structure factor, serves to diminish the height of the prepeak. We find that essentially the same quality of overall fit as measured by χ^2 is achieved for minimum approach values 2.55 $\mathring{A} < r_{CuCe} < 2.9$ $\mathring{A}$, although inspection of the post-simulation CuCe partial $g(r)$ shows that, for $r_{CuCe} < 2.9$ $\mathring{A}$, the partial looks rather unnatural and probably unphysical; we believe that the weighting of the CuCe partial is just large enough to yield an adequate fit. $S_{CeCe}(Q)$, on the other hand, was not well modelled by the RMC method due to the relative lack of information about it in the experimental $S(Q)$, and will not be discussed further. The main peak of the CuCe partial $S(Q)$ is at 3 $\mathring{A}^{-1}$, and the CuCu peak is at 2.5 $\mathring{A}^{-1}$.

Fourier transformation of the RMC partial structure factor of CuCu yields $g_{CuCu}(r)$ with a main peak at 2.5 $\mathring{A}$ (figure 7); the high-r side of this peak is significantly less sharply inclined than the low-r side, and perhaps indicates the presence of a shoulder, or nearby smaller peak at a value of about 2.9 $\mathring{A}$, in agreement with the Gaussians fitted to the experimental $g(r)$. The next peak at 4.4 $\mathring{A}$ is still quite strong, and 4.4 $\mathring{A}$ is precisely a CuCu distance in the crystalline solid. The RMC partial $g_{CuCe}(r)$ (not displayed) is peaked at 2.9 $\mathring{A}$, close to the CuCe distances of 3–3.4 $\mathring{A}$ seen in the crystalline solid.

RMC analysis has also allowed an examination of the bond-angle distributions; we expect the simulated CuCuCu bond angles to be most reliable because of the exceptional

Figure 7. The RMC partial pair correlation function, $g_{CuCu}(r)$, for liquid Cu_6Ce: dashed line: results from a simulation starting from a random initial configuration; solid line: results from a simulation starting from the crystalline initial configuration.
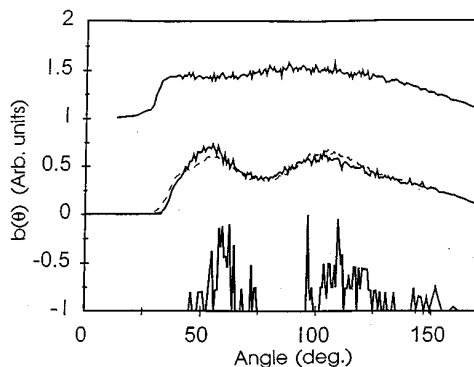
Figure 8. The RMC CuCuCu bond-angle distribution for Cu_6Ce. Uppermost line: the bond-angle distribution of the initial random arrangement. Middle line: the bond-angle distribution at the conclusion of the RMC simulation for the initially random arrangement (solid line), and initially crystalline arrangement (dashed line). Bottom line: the bond-angle distribution for the initially crystalline configuration.

weight of CuCu correlations in $S(Q)$. An examination of the pre-simulation bond-angle distribution for the initial random configuration subjected only to moving out of the particles to minimum distances of approach, and using an atom–atom separation cut-off of 4 Å, showed a rather flat distribution (figure 8), indicative of a random arrangement. The post-simulation angle distribution with a similar cut-off shows a peak at about 55°, and a somewhat broader peak at around 105°; interestingly, crystalline Cu_6Ce has bond angles in a range around 60° and 110°, but a lack of bond angles in between; the post-simulation bond-angle distribution reflects the fact that there are fewer bonds in this same region. There is, however, no evidence in the liquid of the much less common 140° angles also seen in the crystal.

Several possible explanations for NTCs in alloy systems exist, but the results for the present systems appear to provide an unusual challenge. Divalent pure liquid metals and liquid alloys often display a NTC. This behaviour for pure metals occurs as a result of the temperature dependence of the main peak in the structure factor, $S(Q)$, and is seen uniquely

for divalent liquids because of the relative positions of $2k_F$ (where k_F is the Fermi wave vector) and this primary peak in $S(Q)$ [11]. A similar situation occurs for liquid alloys. This characteristic NTC has been seen for liquids with rather low values of ρ, as in our alloys, but is seen only if the effective valence of the liquid is close to 2 [12]. If we assume that La and Ce each contribute three electrons per atom to the conduction band, and Cu and Ag contribute one, then $Z_{\text{eff}} = 1.3$ for Cu_6Ce and Cu_6La and 1.5 for $CeAg_3$, rather too far from 2 to show divalent character.

NTCs are also expected and observed for liquid and amorphous metals, and alloys for which E_F falls approximately at a fairly deep minimum in the density of states (DOS). Fresard, Beck, and Itoh [13] examine this model and further assume non-degeneracy of the conduction electrons (i.e., that $\mathrm{d}f_{FD}/\mathrm{d}E$ evaluated at E_F cannot be approximated by a δ-function—an assumption that is particularly important at high temperatures—where f_{FD} is the Fermi–Dirac distribution function), but take only elastic scattering into account, and find that they obtain a NTC at high temperatures even in this case, but only for $\rho > 400\ \mu\Omega$ cm. They take this to be a possible explanation (at high temperatures) of the behaviour that has come to be called the Mooij correlation: a NTC associated with large ρ. However, they also found that in such cases the thermopower is especially sensitive to features in the DOS. Our experimental thermopower and resistivity show no signs of the behaviour predicted by this model.

If the NTC results from the release of electrons into the conduction band from covalent or ionic bonds as the temperature increases, one often observes a negative minimum in $\alpha(c)$ accompanying a maximum in $\rho(c)$. These NTCs also tend to be quite sharply concentration dependent and to occur at compositions corresponding to maxima in the respective melting curves, and to rather strongly bound crystal structures in the solid alloy. While the NTCs that we see for liquid Cu–Ce and Ag–Ce do occur at maxima in their melting curves, and these also do correspond to preferred solid crystal structures, no feature is apparent in $\rho(c)$ at these compositions that would reflect evidence for bound clusters in these liquids. Moreover, ρ at these compositions is quite low ($\sim$100 $\mu\Omega$ cm), and reaches its peak at much higher RE concentrations.

Salmon [9] has discussed the importance of the position, width, and height of the first sharp diffraction peak for liquids. Significantly, the width of the peak has proved in several cases to be directly related to the r-space distance over which CSRO is present, and the height of the peak to the amplitude of the density fluctuations in $g(r)$. The height of the prepeak in the RMC $S_{\text{CuCu}}(Q)$ suggests that the density fluctuations are not large. Also, the width implies that the order diminishes quickly with distance in the liquid. Such weak order is quite consistent with the absence of features in ρ or S. We suggest that α is perhaps a more sensitive indicator of CSRO than ρ or S, and that the NTCs for Cu–Ce and Ag–Ce are indicative of ordering in those systems. We turn, for an example of this sensitivity, to the liquid Al_2Ca system [14], which also has a small value of ρ ($<$150 $\mu\Omega$ cm) and a NTC ($\alpha = -9 \times 10^{-4}\ °C^{-1}$). The resistivity in this case is also featureless and metallic, as is the thermopower; however, the substitution of Ga for Al gives strong evidence that clusters of Al_2Ca do exist in this system.

Perhaps the strongest single argument in favour of CSRO in liquid Cu_6Ce is the close similarity of the CuCuCu bond-angle distributions for the RMC-generated data and the crystalline material (figure 8). The cluster of bond angles in the liquid near $55°$ compares well with the crystalline configuration, which is peaked slightly closer to $60°$. It is unlikely that these angles result merely from close packing in the liquid, because of the substantial size difference between Cu and Ce atoms (about 50%). It is also clear from examination of the arrangement of atoms in the crystal that bond angles near 115–$120°$, at least for the

crystal, are quite independent of those at $60°$ (not necessarily $2 \times 60°$). Perhaps those near $110°$ in the liquid are similarly independent.

We have argued that CSRO does occur in liquid Cu_6Ce. This implies that CSRO can be seen even in liquid alloys with $\rho < 100$ $\mu\Omega$ cm. The magnitude of the NTC and the height and width of the prepeak of the structure factor indicate that perhaps only a small fraction of the atoms participate in clustering on average, which could explain the lack of discernible features in ρ or S. It is significant that no signs of a prepeak are seen for $S_{CuCu}(Q)$ for liquid $Cu_{0.75}Ce_{0.25}$ [3], even though this concentration is comparatively close to Cu_6Ce. A shallow minimum can be seen in Waseda's partial $S_{CeCu}(Q)$ at 1.6 $Å^{-1}$, but it cannot compare in depth to the minimum modelled in our RMC calculations. It might be reasoned that weak ordering occurs in a reasonably narrow concentration range around stoichiometry; this is consistent with the narrowness of the minimum in α. The chemical similarity with other alloys of Cu with the light rare earths, and the similarity of α for liquid Cu–La, invite further study into possible ordering in these alloys, and possibly alloys of REs with other noble metals.

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