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# Chemical short-range order and the Meyer–Neldel rule for liquid alloys: AlCa and GaAlCa

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**Abstract.** We have measured the electrical resistivity,  $\rho$ , its specific temperature dependence,  $\alpha \equiv (1/\rho) d\rho/dT$ , and the thermopower,  $S$ , of two series of ternary liquid alloys:  $\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$  and  $\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$ . We also provide new analysis for the binary liquid alloy AlCa. We do not see the unusually large values for  $S$  that were found earlier for amorphous *solid* ternary alloys of the approximate composition  $\text{Ga}_x\text{Al}_y\text{Ca}_{60}$ . We do find that, while chemical short-range order (CSRO) appears to occur in the liquid binary alloy  $\text{Al}_2\text{Ca}$ , CSRO is apparently destroyed by substitution of one Ga atom for one Al per complex:  $\text{Ga}_1\text{Al}_1\text{Ca}_1$ . CSRO may exist in the liquid alloy  $\text{Ga}_2\text{Ca}$ . And we find that the activated conductivities of these ternary liquid alloys (and also of liquid AlCa) are consistent with the Meyer–Neldel rule (MNR), extending the range of applicability of the MNR to systems with activation energies about an order of magnitude smaller than previously observed. These results appear to rule out two physical models as universal bases for the MNR, but are consistent with one based on a hopping conductivity whose characteristic energy is that of a polaron shift.

## 1. Introduction and theory

Recent measurements [1] of the electrical resistivity,  $\rho$ , its specific temperature dependence,  $\alpha$  ( $\alpha \equiv (1/\rho) d\rho/dT$ ), and the thermoelectric power,  $S$ , of the liquid alloys AlCa and AlBa provide strong evidence for chemical short-range order (CSRO) in these alloys at the composition  $\text{Al}_2\text{X}$ , where  $\text{X} = \text{Ca}, \text{Ba}$ . This observation is unusual in that the constituent elements in these alloys are all non-transition metals; theoretical calculations, on *amorphous* AlCa [2, 3], however, imply that the electronic structure of this alloy becomes quite non-free-electron-like near  $E_F$ , and that there is evidence of strong Al–Ca bond formation of electronic character at the concentration  $\text{Al}_2\text{Ca}$  [3]. It is not surprising that *liquid* AlCa should have similar characteristics. The rather sharp negative minimum observed in the concentration dependence of  $\alpha$  for liquid AlCa at the composition  $\text{Al}_2\text{Ca}$  is therefore a result of thermal activation of electrons from these bonds into the conduction band.

It is interesting to consider what would happen to the electronic properties of liquid  $\text{Al}_2\text{Ca}$  if isoelectronic Ga were substituted for some or all of the Al in this alloy. For this purpose, we note that both pure liquid Al and pure liquid Ga are trivalent and that their atomic diameters are very nearly the same. (The nearest-neighbour distances in the pure liquids, as obtained by Fourier inversion of their x-ray structure factors, are:  $r(\text{Al}) = 2.79 \text{ \AA}$  and  $r(\text{Ga}) = 2.77 \text{ \AA}$  [5].) The free-electron Fermi energies,  $E_F$ , of these pure liquids are also approximately equal:  $E_F(\text{Al}) = 0.381 \text{ au}$  and  $E_F(\text{Ga}) = 0.365 \text{ au}$ . Pure liquid Ca provides

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a contrast to these two very similar metals:  $r(\text{Ca}) = 3.75 \text{ \AA}$ , and  $E_F(\text{Ca}) = 0.160 \text{ au}$ . We expect that, if Ga is substituted for all of the Al in the liquid alloy  $\text{Al}_2\text{Ca}$ , relatively little change may occur either in the physical structure or the electronic properties of the alloy. In particular, since liquid  $\text{Al}_2\text{Ca}$  shows characteristics of CSRO, perhaps  $\text{Ga}_2\text{Ca}$  will as well. It is not so clear, however, what to expect when perhaps half of the Al atoms have on average been replaced by Ga atoms, as in  $\text{GaAlCa}$ . We report these measurements in the present paper.

It has also been reported [4] that, for *amorphous*  $\text{Ga}_{20}\text{Al}_{20}\text{Ca}_{60}$  (and, to a somewhat lesser extent for  $\text{Ga}_{10}\text{Al}_{30}\text{Ca}_{60}$ ), the measured thermopower,  $S$ , is unusually large, having a magnitude of about  $10 \mu\text{V } ^\circ\text{C}^{-1}$ ; this was hard to understand considering that the components are all simple non-transition metals. In the present study we look for an unusual magnitude for  $S$  in the *liquid* ternary alloy at nearly the same composition.

In the last decade, in a different but yet related study, there has been an interesting discussion of the possible physical origins of the so-called Meyer–Neldel rule (MNR). This was first identified in 1937 by Meyer and Neldel [6]; it is now clear that this empirical rule applies to many properties that show thermal activation in quite different systems; these include crystalline, amorphous, and liquid semiconductors. Applied to a thermally activated electrical conductivity,  $\sigma$ , where

$$\sigma = \sigma_0 \exp\left(-\frac{E}{kT}\right) \quad (1)$$

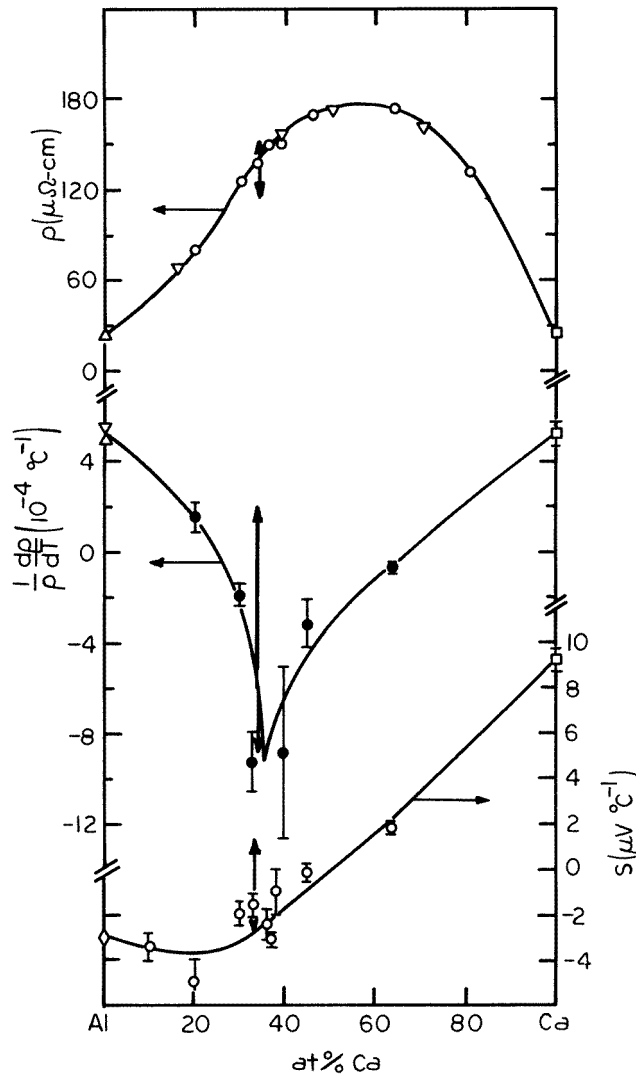
the MNR notes that the following relation exists between  $\sigma_0$  and  $E$  for a class of similar materials:

$$\sigma_0 = \sigma_{00} \exp\left(\frac{E}{\varepsilon}\right). \quad (2)$$

Here  $E$  is a measure of the activation energy,  $T$  is absolute temperature, and  $\sigma_{00}$  and  $\varepsilon$  are constants for the given class of materials. (We note with Fortner *et al* [7] that the value of  $E$  obtained from fitting experimental data to equation (1) is not necessarily equal to the true activation energy.) Typically, for solid or liquid semiconductors, with  $d\sigma/dT > 0$  (or  $d\rho/dT < 0$ ),  $\sigma < 500 \Omega^{-1} \text{ cm}^{-1}$ . Interestingly, for liquid semiconductors, values of  $\varepsilon$  fall into three ranges for eight different alloy systems: (1)  $30 \text{ meV} < \varepsilon < 40 \text{ meV}$ ; (2)  $90 \text{ meV} < \varepsilon < 125 \text{ meV}$ ; and (3)  $\varepsilon \simeq 180 \text{ meV}$  [7].

One rather common suggestion for a physical basis of the MNR involves the statistical shift of the Fermi energy,  $E_F(T)$ , with temperature [8]. As noted by Fortner *et al* [7], this explanation requires that  $kT/\varepsilon < 1$  to avoid the non-physical result of a negative activation energy,  $E$ . Fortner *et al* [7] show that several liquid semiconductors have  $kT/\varepsilon > 1$ , ruling this out as a universal explanation of the MNR.

Another possible explanation of the MNR is based on multiphonon hopping, for which, as the number,  $N$ , increases (where  $N$  is the number of phonons that are involved in the promotion of a single electron to higher energy,  $E$ ), the number of excitation paths increases exponentially, and the MNR results [9, 10]. For this, in terms of our parameters, we have  $N\varepsilon \simeq E$ , with  $N \gg 1$ . This implies that  $\varepsilon \ll E$  for MNR to be observed for a given system. Fortner *et al* [7] also assume a variant of this hopping conductivity, but one for which the characteristic energy,  $w$ , is that of a polaron; a system that exhibits a strong polaron effect, appropriate for a flexible structure, may also exhibit MNR effects (for  $w > E/2$ ) even at high temperatures. Interestingly, the characteristics of  $\sigma(T)$  for three of the liquid alloy systems reported here allow us to test these explanations for the MNR in a region of parameter space not previously explored.



**Figure 1.** Measurements of  $\rho$ ,  $\alpha$  ( $\alpha \equiv (1/\rho)d\rho/dT$ ), and  $S$  for the liquid alloy AlCa as a function of Ca concentration on the isotherm  $T = 1079^\circ\text{C}$  (from reference [1]). The vertical arrows indicate the range of values taken by these parameters for the ternary alloy  $\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$ .

## 2. Experimental method

The base material of which the alloys were made was obtained from the Atomergic Chemetals Corporation (99.999% Al), and from Aesar/Johnson-Matthey (99.99% Ca and 99.999% Ga). Before the Ca was used, however, it was encapsulated in Ta and baked at high temperature and in high vacuum for three days to remove the hydrogen that normally contaminates the alkaline earths. The material was then cut and the samples assembled under an argon atmosphere in an evacuable glove box. Measurements were then made on alloys held in high-density  $\text{Al}_2\text{O}_3$  tubes; contact to the liquid sample was made via holes

drilled into the tubes and sealed with graphite plugs. A molybdenum stirring wire permitted vigorous agitation of each alloy to ensure homogeneity. In other respects, the measurement techniques were similar to those reported earlier [11].

### 3. Results

Experimental results for  $\rho$ ,  $\alpha$ , and  $S$  for the liquid binary alloy AlCa are shown in figure 1. These were reported and discussed earlier [1], but the figure is repeated here because this forms the base system on which the ternary alloys are formed. (These data are also used in a test of the MNR.) The deep and sharp minimum in  $\alpha$  at about 33 at.% Ca provides partial evidence for the CSRO at the concentration  $\text{Al}_2\text{Ca}$  which has also been described [1]. The vertical arrows in the figure show the range of values which the parameters take on as Ga replaces Al in the alloy while the Ca content is held at 33 at.%. (Some data for  $\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$  have also been obtained, but, because the changes are small, the range of values is not shown in figure 1.)

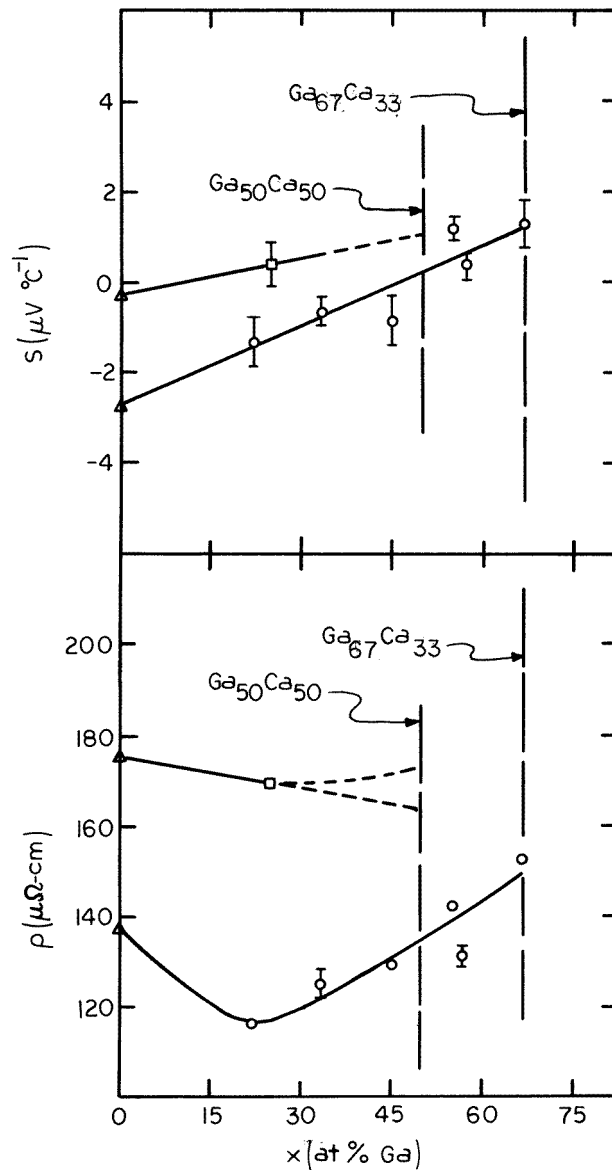
Measurements of  $S$  and  $\rho$  for the ternary liquid alloy systems  $\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$  and  $\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$  are shown in figure 2. All data are for the 1079 °C (1352 K) isotherm, as are those in figures 1 and 3. The variation of  $S$  with the Ga concentration,  $x$ , is monotonic and featureless;  $d\rho/dx$ , however, is negative for small  $x$  for both systems, and appears to rise to zero for  $\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$  when about one-third of the Al atoms have been replaced by Ga.

Measurements of  $\alpha(x)$  for the same two liquid ternary alloy systems are shown in figure 3. Again, the variation of  $\alpha(x)$  for the alloy  $\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$  is probably small, but  $\alpha(x)$  for  $\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$  shows interesting structure, with  $\alpha(x)$  becoming less negative rapidly for small  $x$ , displaying a maximum at about 45 at.% Ga, followed by a shallow minimum at about 55 at.% Ga. In each case in figures 2 and 3, vertical broken lines indicate concentrations at which all Al atoms in that alloy have been replaced by Ga.

### 4. Discussion

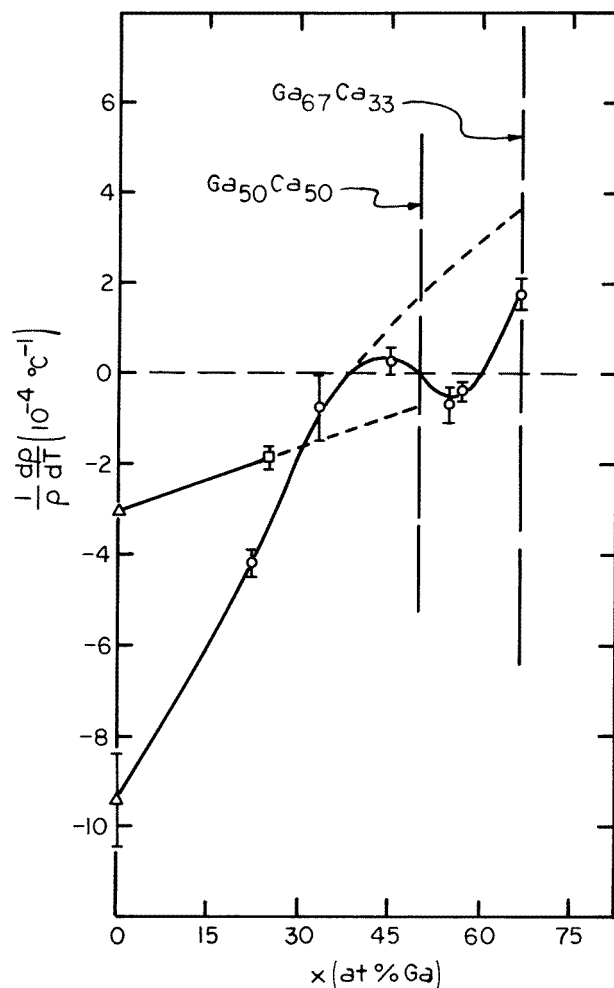
We note immediately that we see no unusual magnitude for  $S$  at any concentration for either liquid ternary alloy system; in particular,  $S \cong 0$  for the alloy  $\text{Ga}_{25}\text{Al}_{25}\text{Ca}_{50}$ , a concentration close to that for which the amorphous alloy showed an unusually large magnitude [4] (see figure 2). Moreover, we also note that while  $dS/dx$  has the same sign for the ternary liquid and the amorphous solid alloys, its magnitude for the liquid alloys is about an order of magnitude smaller.  $d\rho/dx$ , for small  $x$ , differs between these solid and liquid alloys *both* in sign *and* in magnitude:  $d\rho/dx \cong -0.3$  for liquid  $\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$ , whereas  $d\rho/dx \cong +5.5$  for amorphous  $\text{Ga}_x\text{Al}_{40-x}\text{Ca}_{60}$ , where the units are  $\mu\Omega \text{ cm/at.}\%$  [4]. And, significantly, although  $\alpha$  and  $d\alpha/dx$  are of about the same magnitude for these same solid and liquid systems, the  $d\alpha/dx$  are of opposite sign. We offer no explanation for the difference between our results and those for the amorphous alloy other than to note that the electronic properties of amorphous solids often reflect the fabrication methods employed. (Naugle *et al* [4] also comment on expected intrinsic differences in short-range order between liquid and glassy alloys.)

Perhaps of greater interest is what appears to happen to the CSRO in liquid  $\text{Al}_2\text{Ca}$  as Ga replaces the Al in this alloy.  $\rho(x)$  initially decreases with increasing Ga content, and  $\alpha(x)$  becomes less negative rapidly as Ga is first added. Both of these (especially the  $\alpha(x)$  dependence) suggest that the  $\text{Al}_2\text{Ca}$  CSRO association is disrupted rapidly as Ga



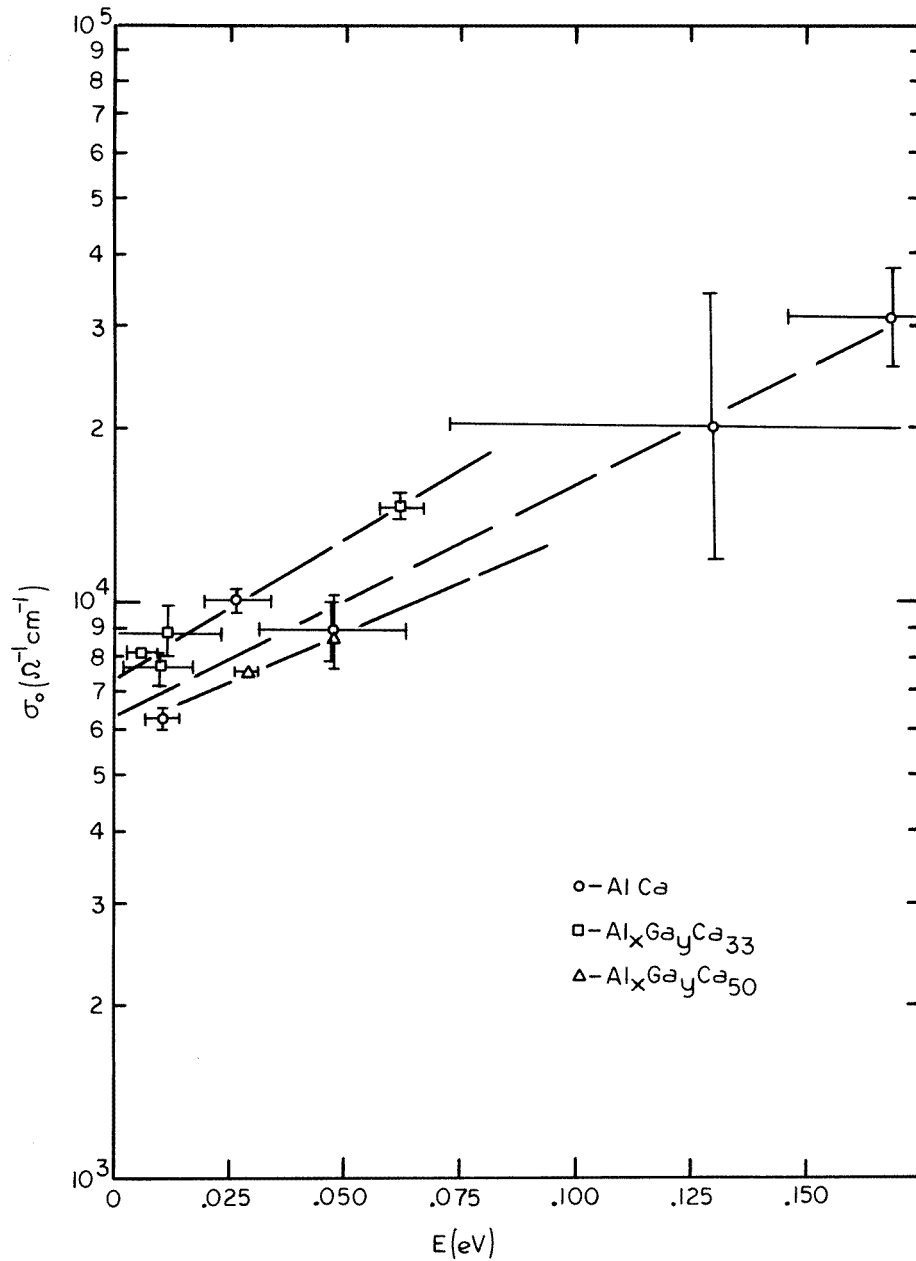
**Figure 2.** Measured values of  $S$  and  $\rho$  for two series of ternary liquid alloys (at  $T = 1079^\circ\text{C}$ ):  $\circ$ :  $\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$ ; and  $\square$ :  $\text{Ga}_x\text{Al}_{50-x}\text{Ga}_{50}$ . (The dashed lines show possible extrapolations beyond the data.)  $\Delta$ : from reference [1]. The vertical lines show the Ga concentration, for each alloy, at which the Al concentration goes to zero.

is added to the binary alloy. This implies that no complexes of the type  $\text{Ga}_1\text{Al}_1\text{Ca}_1$  are electronically preferred, and none form, even temporarily. We also note that, if one does a simple statistical calculation in which Ga atoms randomly replace Al atoms in an assemblage of  $\text{Al}_2\text{Ca}$  'molecular' complexes, 50% of these  $\text{Al}_2\text{Ca}$  complexes will have at least one Al replaced by Ga when the Ga concentration reaches 19 at.% ( $\text{Ga}_{19}\text{Al}_{48}\text{Ca}_{33}$ ), and 80% will



**Figure 3.** Measured values of  $\alpha$  ( $\alpha \equiv (1/\rho)d\rho/dT$ ) for the two series of ternary liquid alloys (at  $T = 1079^\circ\text{C}$ ):  $\circ$ :  $\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$ ;  $\square$ :  $\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$ . (Dashed lines are possible extrapolations—see the text.)  $\triangle$ : from reference [1]. The vertical lines show the Ga concentration, for each alloy, at which the Al concentration goes to zero.

have at least one Al atom replaced by Ga at 33 at.% Ga ( $\text{Ga}_{33}\text{Al}_{33}\text{Ca}_{33}$ ). This calculation, coupled with the observation that  $\alpha(x)$  has increased to nearly zero by  $x = 33$  at.% Ga (see figure 3), also suggests that no complex of the type  $\text{Ga}_1\text{Al}_1\text{Ca}_1$  is favoured. On the other hand, however, the ultimate decrease in  $\alpha(x)$  and subsequent minimum (for large  $x$ ) at least suggests that CSRO complexes of the type  $\text{Ga}_2\text{Ca}$  *do* form, as do those of the type  $\text{Al}_2\text{Ca}$ . The formation of these  $\text{Ga}_2\text{Ca}$  complexes would hold  $\alpha(x)$  low for large  $x$  (figure 3 shows  $\alpha(x)$  well below the extrapolation from the low- $x$  region (dashed line) up to large  $x$ ); moreover, the measured value of  $\alpha$  for the binary liquid alloy  $\text{Ga}_2\text{Ca}$  (about  $2 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ ), shown in figure 3, is far below the value of perhaps  $8 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  that one expects for pure Ga, based on measurements made at lower temperatures [12]. It appears, therefore, that  $\alpha(x)$  may perhaps also be at a minimum at  $\text{Ga}_2\text{Ca}$  for the liquid alloy  $\text{Ga}_x\text{Ca}_{100-x}$ , as



**Figure 4.** A semilogarithmic graph of  $\sigma_0$  versus  $E$  for parameters obtained from a fit of the measured data for the three alloy systems to equation (1).

is the case for  $\text{Al}_2\text{Ca}$ ; this is also consistent with  $\text{Ga}_2\text{Ca}$  complex formation (see figure 1). It would be interesting to extend the calculations of Hafner and Jaswal [3] to both liquid  $\text{Ga}_2\text{Ca}$  and liquid  $\text{Ga}_1\text{Al}_1\text{Ca}_1$  to look for evidence for bond formation in the former and

**Table 1.** Values of the parameters obtained from a fit of our  $\sigma(T)$  to the MNR.

Liquid alloy	$E$ -range ( $10^{-2}$ eV)	$\sigma_0$ -range ( $10^4 \Omega^{-1}\text{cm}^{-1}$ )	$\varepsilon$ (meV)	$\varepsilon/E$	$\sigma_{00}$ ( $10^4 \Omega^{-1}\text{cm}^{-1}$ )	$kT/\varepsilon$
$\text{Al}_x\text{Ca}_{100-x}$	1.1–17	0.6–3.1	$108 \pm 13$	0.6–10	0.63	1.06
$\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$	0.6–6.2	0.8–1.5	$119 \pm 9$	1.9–20	0.74	0.96
$\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$	2.8–4.8	0.75–0.88	127	2.6–4.5	0.60	0.90

lack of it in the latter.

Finally, as noted in the introduction, our measurements on the liquid alloys  $\text{Al}_x\text{Ca}_{100-x}$ ,  $\text{Ga}_x\text{Al}_{67-x}\text{Ca}_{33}$  and  $\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$  allow us to make an interesting new test of the physical origins of the MNR. We recognize that, because our data for  $\sigma(T)$  span a range of only 100–200 °C at about 1100 °C (1373 K), a variety of functional forms could be assumed for  $\sigma(T)$ ; we nonetheless can fit our data for these three alloys to equation (1), and we do this. A least-squares analysis of  $\ln \sigma$  versus  $1/T$  yields a set of straight lines with correlation coefficients ranging from about 0.6 to greater than 0.95. These coefficients are reflected in the error bars displayed in figure 4. All of the data for which  $\alpha < 0$  were used. We plot the values of  $\sigma_0$  versus  $E$  that were obtained from these fits on a semi-logarithmic graph, figure 4, to test for adherence to the MNR. We note from figure 4 that the fit of these data to the form of equation (2) is reasonably good, and is certainly not worse than it is for several other systems (see reference [7]). Numerical values of  $\varepsilon$  and  $\sigma_{00}$  obtained from this fitting procedure are shown in table 1. Note that we have only two data points for the alloy  $\text{Ga}_x\text{Al}_{50-x}\text{Ca}_{50}$ , and that the range of values of  $\sigma_0$  and  $E$  for this alloy is also small; the results of the analysis for this alloy are therefore not of the statistical quality that they are for the other two.

We see (table 1 and figure 4) that not only are these data consistent with the MNR, but the parameter  $\varepsilon$  places all three alloys into the same class of materials: those with  $\varepsilon$  in the range  $90 \text{ meV} \leq \varepsilon \leq 125 \text{ meV}$ . It is interesting that these liquid alloys yield the same value of  $\varepsilon$  as do a class of solid and liquid semiconductors which have values of  $\sigma_0$  and  $\sigma_{00}$  one to two orders of magnitude smaller. Moreover, the range of values that we find for  $E$  (a measure of activation energy) is in many cases at least an order of magnitude smaller than it is for the liquid semiconductors [7], and for other systems that have shown MNR behaviour. Thus we have apparently extended the range of applicability of the MNR for the first time to systems that have activated conductivities that are in the metallic range. (We note that these alloy systems, though metallic, have conductivities that are too low for the free-electron model to apply.)

The magnitudes which we obtain for  $\varepsilon$  and  $E$  appear to rule out the multiphonon hopping model of Yelon *et al* [9, 10] as a universal mechanism, since  $\varepsilon$  is not substantially less than  $E$  for these systems (see table 1). As was the case for the liquid semiconductors [7], we find  $kT/\varepsilon \sim 1$  (and perhaps  $>1$  in one case), making it unlikely that the statistical shift in  $E_F$  with temperature can be a universal mechanism for the MNR. Only the model of Fortner *et al* [7], which posits a hopping conductivity, but whose characteristic energy is that of a polaron shift, appears to be consistent with our results. And, as also noted by these authors, the flexibility of a temporary CSRO complex in a liquid such as we have examined is expected to be quite high, making this mode reasonable. (Fortner *et al* [7] draw on the earlier theoretical work of Mott and Davis [13] and Emin [14] in their development of the MNR via a hopping conductivity.) It is difficult, however, to understand how a hopping conductivity mechanism may be active in the conductivity regime of our measurements.

## Acknowledgment

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