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LIQUID TELLURIDES: STRUCTURE AND PROPERTIES

Marie-Louise Saboungi, J. Fortner, J. W Richardson,
A. Petric[1], M. Doyle[2], and J. E. Enderby[3]

Argonne National Laboratory
Argonne, IL 60439

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[1] McMaster University, Hamilton, Canada

[2] Division of Educational Programs, Northwestern University, Evanston, IL

[3] H. H. Wills Physics Laboratory, University of Bristol, United Kingdom

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*Permanent address: McMaster University, Hamilton, Canada **Participant from Division of Educational Programs; Present address: Northwestern University, Evanston, Ilinois ***Permanent address: H.H. Wills Physics Laboratory, University of Bristol, Bristol BSS 1TL (UK).

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Argonne, Illinois 60439

*Permanent address: McMaster University, Hamilton, Canada

**Present address: Northwestern University, Evanston, Ilinois

***Permanent address: H.H. Wills Physics Laboratory, University of Bristol, Bristol (UK).

Abstract

In this paper a review of the thermodynamic, electrical and structural properties of liquid alkali-tellurium alloys is presented with a special emphasis on the interplay between these properties. The thermodynamic properties indicate ordering of the solutions at compositions corresponding to about 12, 50, and 67 atom% of alkali atoms. The electrical conductivity and thermopower data confirm that these liquids are true semiconductors. The neutron diffraction patterns coupled with the above information indicate that in the case of liquid $K_{0.12}Te_{0.88}$ the measured structure is dominated by the Te-Te contribution, and is remarkably similar to that of pure liquid tellurium, while the equiatomic alloy $K_{0.50}Te_{0.50}$ is shown to contain mostly Te pairs which are identified with Zintl ions, Te_2^{2-}.

1.Introduction

Of the chalcogen elements tellurium is perhaps the least understood.[1, 2] Pure liquid ($l-$) Te is a semimetal, whose conductivity places it between the regimes of Ziman scattering theory (metallic) and diffusive (semiconducting) behavior.[3] Further confusion arises from diffraction measurements, where the measured radial distribution function (rdf) shows that there is no well-defined first coordination shell, [1,4] leaving open the fundamental point of whether the number of bonded neighbors is two or three.

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The peculiar structure of pure *l*-Te is often explained as containing a high density of single-bonded (1F) and 3-fold bonded (3F) defects.[2,5] From this point of view, the first peak in the rdf of pure *l*-Te has contributions from long-lived 2-fold (intra-chain) and short-lived 3F (inter-chain) and 1F (chain termination) sites. The 3F and 1F sites are in "fast exchange" as short chains interact. Cutler [2] has proposed a model based on Pauling-type resonance (bond switching) which, while conceptually different, leads to similar behavior. Either view would be consistent with the rapid transition from semimetallic to semiconducting behavior observed when alloying Te with Se [3], Tl [1], or K [6].

Insight into the atomic and electronic structure of pure *l*−Te may be obtained from a better understanding of the role played by Te in liquid semiconducting alloys. In this review, we will emphasize this aspect by focussing on the liquid alkali-tellurium alloys where thermodynamic, electrical conductivity, thermopower, and neutron diffraction measurements have yielded an explanation for the nature of the bonding not only in the alloys but also in *l*−Te.

2.Thermodynamic, Electrical and Structural Properties

a. *Thermodynamic Results*

In our previous study of intermediate-range order, alloys made by combining alkali metals with either Pb, Sn, Bi, or Sb [7,8] showed typical behavior in the thermodynamic properties of mixing, such as peaks at one or two compositions in the excess stability and entropy of mixing and in some cases a strong dependence of the heat capacity of the equiatomic alloys on temperature. The alkali-Te systems pose a challenge to study since little information exists on these alloys and the large electronegativity difference makes direct synthesis difficult. Petric *et al* [9,10] carried an accurate coulometric titration using Na or K substituted β''−Al_2O_3 as a solid electrolyte and measured the electromotive force for various compositions as a function of temperature. Phase diagrams were determined and an equiatomic compound, KTe, was identified. Furthermore, in dilute solutions, the limiting slope of the logarithm of the alkali atom activity was found to be unusually negative and rather large, indicating a tendency for Te to make chains as opposed to heterocoordination. Similar behavior was reported earlier in K-Sb alloys [8] where the presence of chains in the liquid phase of Cs-Sb had been suggested by diffraction measurements [11]. The excess stability, which is an unambiguous indication for ordering in the melt, exhibited two peaks in the case of K-Te (at 12 and 50 atom% K) and a flat shoulder extending from 10 to 20 atom% and a broad maximum at 50 atom% Na in the case of Na-Te (see Figure 1). A third peak, which should be very strong, is expected to occur at the stoichiometric composition (67 at% K or Na) corresponding to A_2Te where the charge transfer leads to an ionic liquid. Despite the scatter in the earlier data of Granstaff and Thompson [12], a strong peak in the excess stability is clearly visible at Na_2Te. To our knowledge, these are the only alloys which exhibit three distinct compositions of ordering in the liquid. In addition, the magnitudes of the peaks, especially in the case of K-Te, are impressively large. The remaining thermodynamic functions of mixing have been derived and discussed by Petric *et al* [9, 10];the entropy of mixing in the vicinity of the equiatomic compound is found to have the lowest known value for any liquid alloy. Even though the values for the excess heat capacity in the liquid vary with composition, their magnitudes are small compared with those of the alkali-lead and alkali-tin alloys [13, 14] but similar to those obtained in K-Sb alloys [8].

b. Electrical Transport Results.

Fortner *et al* [6] have recently measured the electronic conductivity and absolute thermoelectric power of the K-Te system from pure Te to the equiatomic compound. Their results (Figure 2) show that the conductivity σ decreases monotonically with the addition of potassium, exhibiting no particular feature around $K_{.12}Te_{.88}$. The same observation holds for Na-Te where accurate measurements have been performed by Kraus and Glass [15]. However, all liquid alloys containing more than 10 atom% potassium have σ values typical of true semiconductors as defined by Enderby and Barnes [1]. The composition dependence of the conductivity is very large and far outside the realm of Ziman scattering theory. The role of the alkali metal appears to be more than simply diluting Te and affects how Te atoms are arranged. At the equiatomic composition and in the vicinity of the melting point, the electrical conductivity takes an extremely low value, 0.5 $\Omega^{-1}\mathrm{cm}^{-1}$. The temperature dependence of σ has large negative values [6].

The absolute thermopower, S, was measured in the same apparatus as the electrical conductivity. S is positive in pure liquid Te ($\sim 70\mu$V K^{-1}) and increases rapidly with K concentration;it reaches a maximum at 30 atom% K with a value of $\sim 210\mu$V K^{-1} near the melting point, then decreases rapidly with composition; for all compositions, S decreases with temperature. These observations are consistent with the removal of negatively charged 3F defects upon addition of alkali atoms. This removal increases the ratio of holes to conduction electrons while decreasing the total charge carrier concentration. The use of the Kubo-Greenwood formalism to correlate σ and S is underway and should yield information on the dependence of σ on the energy E.

c. *Neutron Diffraction Results*

Time-of-flight neutron diffraction was carried out in the Special Environment Powder Diffractometer at Argonne's Intense Pulsed Neutron Source. Powder diffraction patterns were obtained at room temperature, and liquid diffraction was performed at $\sim$450°C.

The diffraction pattern from the powdered KTe at room temperature confirmed the presence and stability of this compound as inferred from the emf measurements. The structure of KTe was determined from a Patterson Fourier synthesis derived from the integrated intensities of neutron powder diffraction maxima.(Figure 3) Refined lattice parameters are: a = 5.6092(1), c = 12.2180(2) Å, space group: $P6_3/mmc$ (14), Z = 2. In addition to the nearest neighbour Te, each Te atom is surrounded by a trigonally distorted octahedron of K atoms characterized by Te-K distances, 3.521(1),and 3.634(1)$\AA$, and K-Te-K bond angles, $6 \times 76.8^\circ, 3.8^\circ, 3.4^\circ$, and 3.2°. Crystalline K_2Te_2 is isostructural with Li_2O_2, crystallizing in a modified Ni_2In-type close-packed hexagonal structure. In Ni_2In-type structures, half of the octahedral interstitial holes are filled with In and half with Ni. The modified structure has In atoms replaced by pairs of atoms, in this case telluriums (Te-Te = 2.789(3)$\AA$).

The formation of Te_2^{2-} dimers is an essential feature of the structure of KTe. The crystalline structure of a series of tellurides has been studied by x-rays by Böttcher and his group [16, 17]. With the exception of NaTe and LiTe, Te dimers are reported; an unusual structure is obtained for NaTe wich is equivalent to a Na_6Te_6 structural unit, with two separate anionic species Te_5^{4-} and Te^{2-}. The presence of the divalently charged dimer in the other alloys is consistent with the Zintl rule [18], which suggests the formation of Te_2^{2-} anions if the charge transfer from the alkali atom to Te is complete. Indeed, such dimer ions have been identified not only in the crystalline form as indicated above, but also more recently in the vapor phase by Weil and coworkers [19, 20].

Standard programs for intensity, background, absorption, multiple scattering, and inelastic scattering were used to analyse and refine the liquid data data. The measured total structure factors are shown in figure 4. There are major differences in the structures as shown by the first peak, which is located at about 1.2 $Å^{-1}$ for $K_{0.50}Te_{0.50}$ but occurs only as a weak shoulder in the case of $K_{0.12}Te_{0.88}$, and by the alternating positions of the first three extrema thereafter, i.e., a minimum for one composition corresponds to a maximum for the other. The peak at 1.2 $Å^{-1}$ is referred to as the "first sharp diffraction peak," a well-known signature of intermediate-range order in liquid alloys [21] and amorphous systems [22]. Furthermore, it can be shown that in the case of $K_{.12}Te_{.88}$, the K-K contribution is negligible and the K-Te contribution is small, whereas for $K_{.50}Te_{.50}$, each partial pair distribution is substantial.[23] This, coupled with the large difference between Te-Te covalent (~2.8 Å) and K-Te ionic (~3.6 Å) bond lengths, results in the total scattering as almost exclusively representative of the Te interactions with Te or the alkali atom.

The real space functions such as the average radial distribution function n(r) are obtained via Fourier transformation of S(Q). In the present case, n(r) shown in Figure 5 was calculated using $Q = 15\AA^{-1}$ as the experimental cutoff distance. For molten $K_{0.12}Te_{0.88}$, the clear separation of the first peak in the rdf from the rest of the neighbors is significant. A Gaussian fit to the first peak in the pair distribution function T(r), at a distance of 2.78 ± 0.04 Å and having an area of 1.7 atoms, indicates Te chains (about 5 to 10 atoms long) persisting into the melt. The distance corresponds, within experimental error, to the separation 2.74 Å of the molecular ion $(Te_2)^{2-}$ found by Hastings *et al* [24] in solid $MnTe_2$ (an antiferromagnetic semiconductor). It is interesting to note, additionally, that otherwise the rdf is quite similar to that of pure liquid Te, suggesting that the increased order is achieved with only subtle changes to the local environment. A shoulder at 3.6 Å, matching the sum of the K^+ and Te^{2-} ionic radii, can by analogy with comparable data on the liquid Tl-Te system [25] be attributed to the K-Te first coordination sphere.

The $n(r)$ for liquid $K_{0.50}Te_{0.50}$ (Figure 5) shows that there is again a first Te-Te coordination peak at 2.8 Å, having in this case a coordination of 0.96. This virtually complete pairing of tellurium atoms is in sharp contrast to the heterocoordination of liquid CuTe and the partial pairing of selenium in liquid CuSe (Se-Se coordination of ~0.6). [26] It is informative to compare this liquid structure with that of crystalline KTe (figure 3), whose peaks are indicated in the figure by the vertical bars. The covalent Zintl pair, present in both the solid and the liquid, proves to be quite stable, while the ionic structure is loosely preserved, typical of strongly interacting liquids. The large, broad, and asymmetric second peak at about 3.5 Å corresponds to the Te-K shell, providing the expected heterocoordination in an ionic melt. No evidence of ordering at the next-nearest-neighbor level of Te (correlation between Te_2^{2-} ions) is apparent.

Finally, the pronounced first sharp diffraction peak at Q ~ 1.2 $Å^{-1}$ arises from the high concentration of complex Zintl ions, similar to that found in other ordered liquid systems. [21] Its weaker presence in the $K_{0.12}Te_{0.88}$ alloy (and complete absence in pure $l-$Te) is presumably due to the lower concentration of Te_n^{2-} ions.

Discussion

The role of the potassium appears to be that of nearly complete charge transfer to Te . In $K_{.12}Te_{88}$, the additional electrons stabilize the short chains as Te_n^{2-} ions (n~5 – 10). These charged chains will certainly interact much more weakly in aa alloy diluted with K^+ than similar chains in the pure system, which is believed to contain a high density of 1F and 3F defects. The potassium thus effectively quenches the 1F defects by removing the 3F defects. This view is in accord with that of Silva and Cutler [5] for l−Te, who proposed that the electronic and optical properties can be explained by the presence of very short (3 to 4 atoms) covalently bonded, electrostatically interacting chains. The removal of defects on alloying with K is consistent with the decrease in electronic conductivity by more than an order of magnitude (from $2500\Omega^{-1}\text{cm}^{-1}$ to $200\Omega^{-1}\text{cm}^{-1}$) upon alloying (Figure 2). Such a large decrease is inconsistent with the formation of isolated $Te_2{}^{2-}$ ions in a Te matrix for which scattering theory would predict much smaller conductivity changes. The above interpretation would explain the extra feature in the excess stability at 12 atom % alkali metal.

Recent Raman scattering experiments have been performed on KTe in both crystalline and liquid states. [27] The spectra at room temperature are characterized by the presence of a strong peak at 170 cm^{-1} which is identified with the vibrations of the Te_2^{2-} dimers. This peak broadens and decreases in intensity upon melting while its position remains unchanged. Such a behavior is reminiscent of the melting process in YCl_3 where the octahedral network is preserved in the liquid state.[28] The interesting case of NaTe remains to be studied since dimers do not appear in the crystalline phase but have been shown to be present in the vapor phase by Weil [20]. Our thermodynamic results coupled with the electrical conductivity of Kraus and Glass [15] suggest a similar behavior of liquid Na-Te to that of K-Te. The fact that the excess stability peaks are less pronounced may suggest a lower stability of the Te dimers as is the case for Pb_4^{4-} or Sn_4^{4-} Zintl ions in NaPb or NaSn compared with KPb or KSn, respectively [7, 13].

Conclusions

Thermodynamic, electrical transport, and neutron diffraction measurements on molten Na-Te and K-Te alloys indicate a high degree of structural ordering at the equiatomic composition and at 12 atom % of alkali atoms. These two compositions form liquid semiconducting alloys. The results, particularly for the dilute system, support the picture of Silva and Cutler for the structure of pure liquid tellurium. Also the first evidence for the appearance of Te_2^{2-} Zintl polyanions is observed as the K concentration is increased. This is consistent with a simple charge-transfer scheme, whereby the Te bonds according to the 8-N rule with N, the number of valence electrons, has the value seven if there is complete charge transfer of one electron from K. The apparent removal of defects in the dilute system may have considerable significance for the semiconducting behavior. We are unaware of any other example of Te pairing in liquid alloys. The most likely candidate for this effect is liquid $MnTe_2$: however, the Te pairing which occurs in the solid, referred to above, was shown to be absent in the liquid directly by structure studies and indirectly by the observed conductivity and thermopower [29]. Neutron diffraction measurements on Na-Te alloys are underway to study both crystalline and liquid structures.

Acknowledgments

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Figure Captions

1. Excess stability in the Na-Te and K-Te alloys from Petric *et al*[9, 10].
2. Electrical conductivity in the Na-Te and K-Te alloys from [6, 15].
3. Structure of crystalline KTe compound.
4. Total structure factors for liquid K-Te alloys: (a) $l-K_{0.12}Te_{0.88}$; (b) $l-K_{0.50}Te_{0.50}$. [23]
5. The total average radial distribution function for (a) $l-K_{0.12}Te_{0.88}$; (b) $l-K_{0.50}Te_{0.50}$. The vertical bars in (b) represent the position of coordination shells in the crystalline phase of KTe.[23]

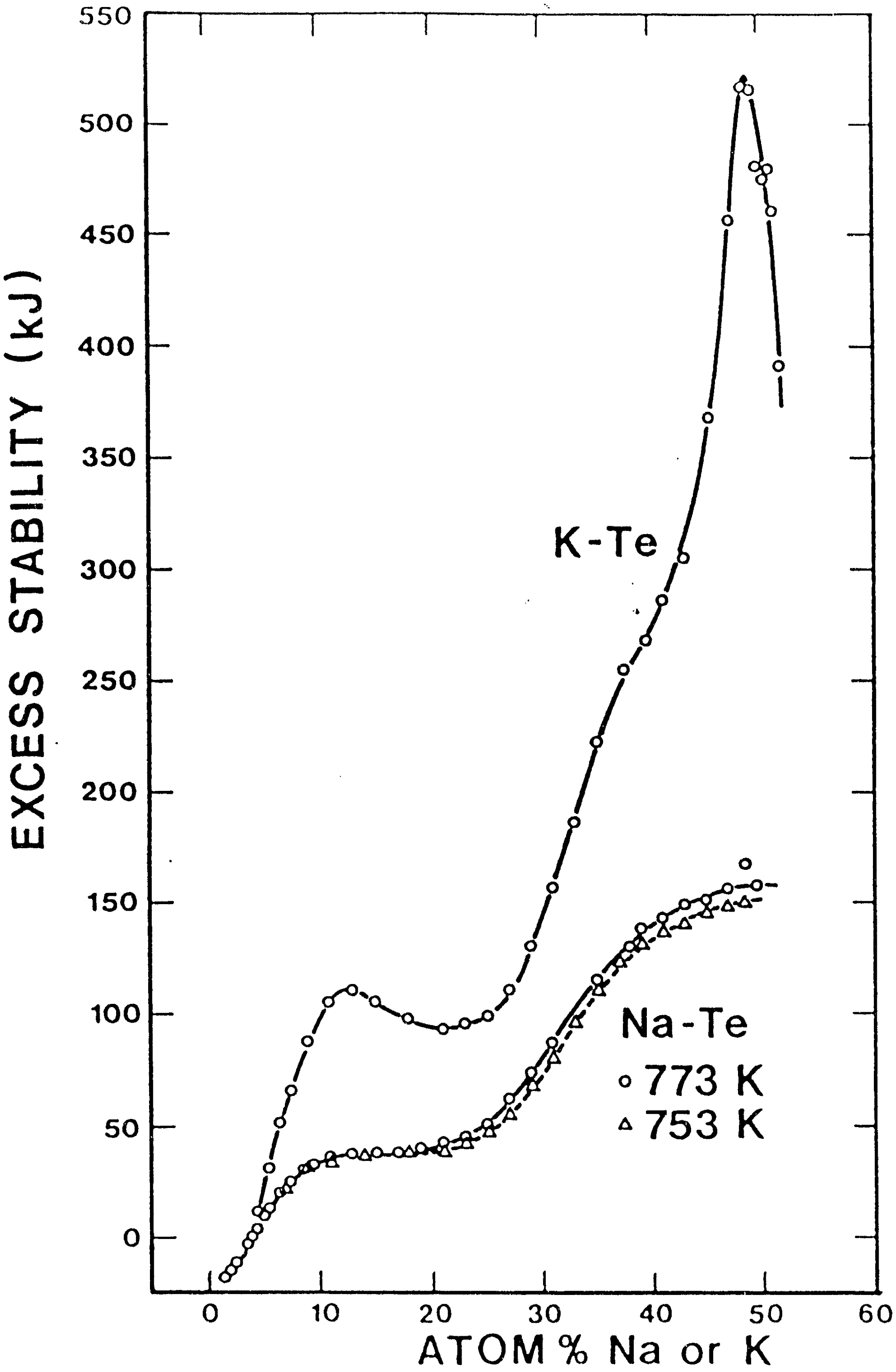
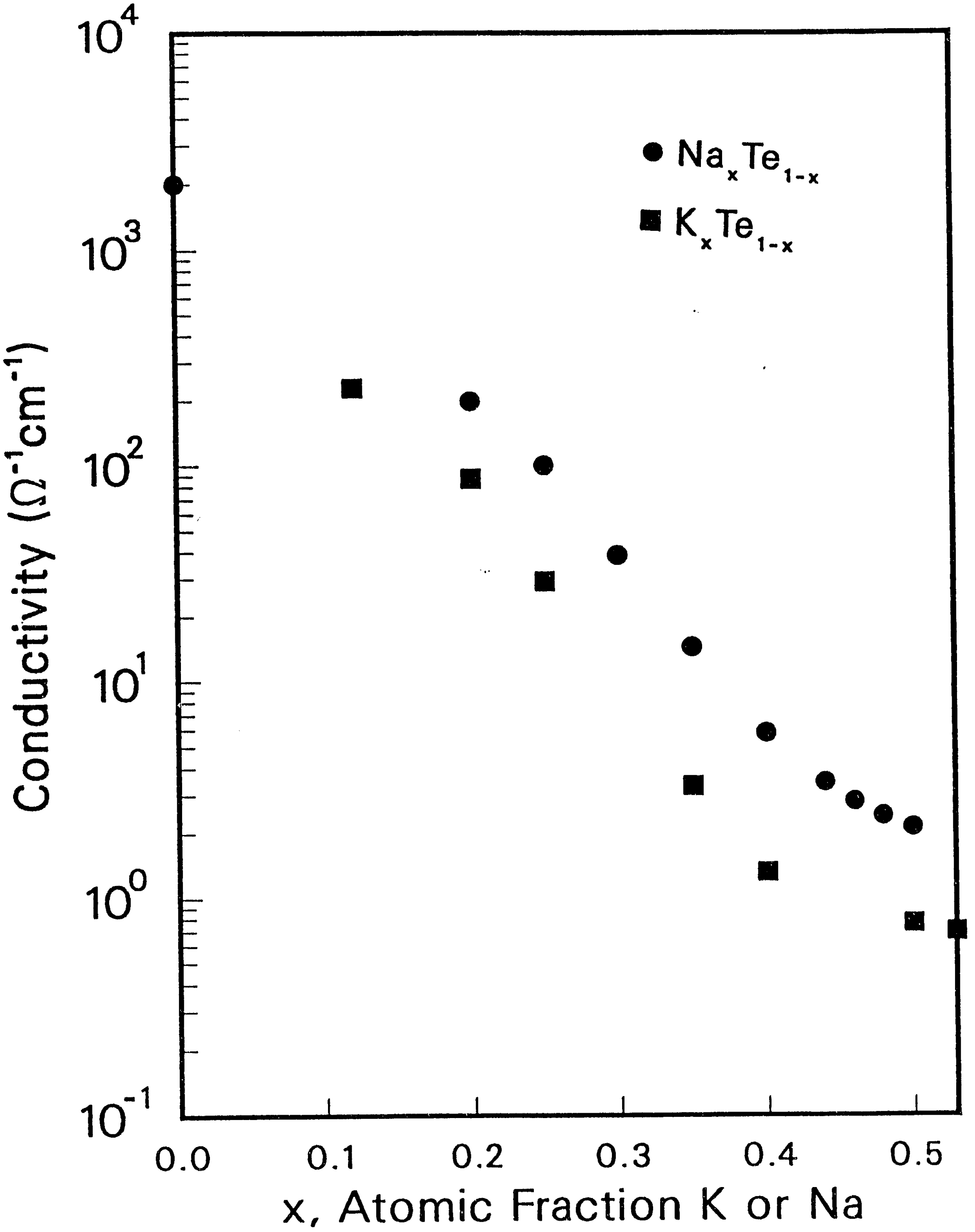
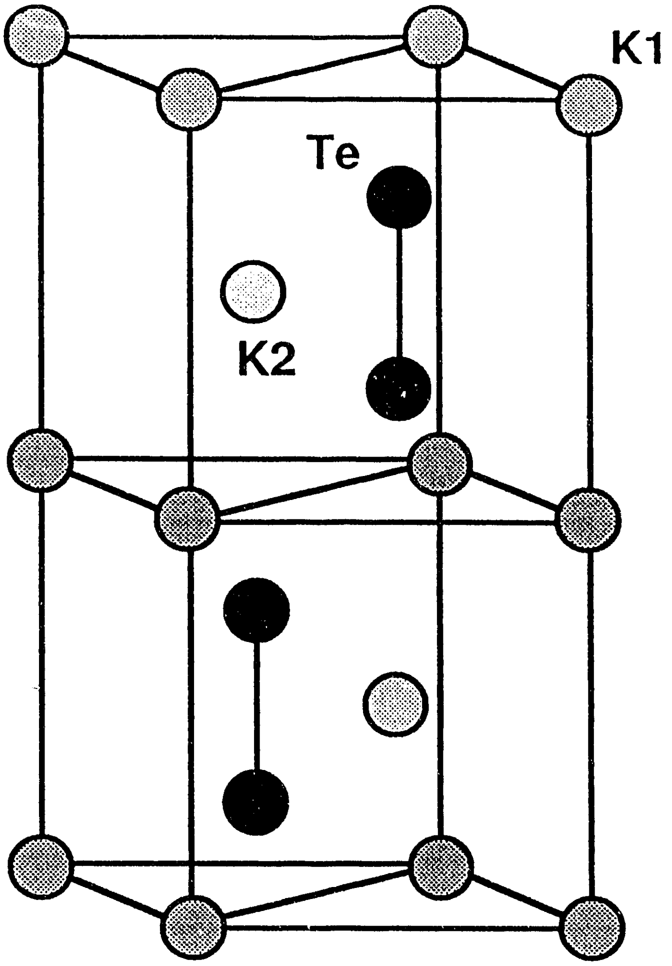


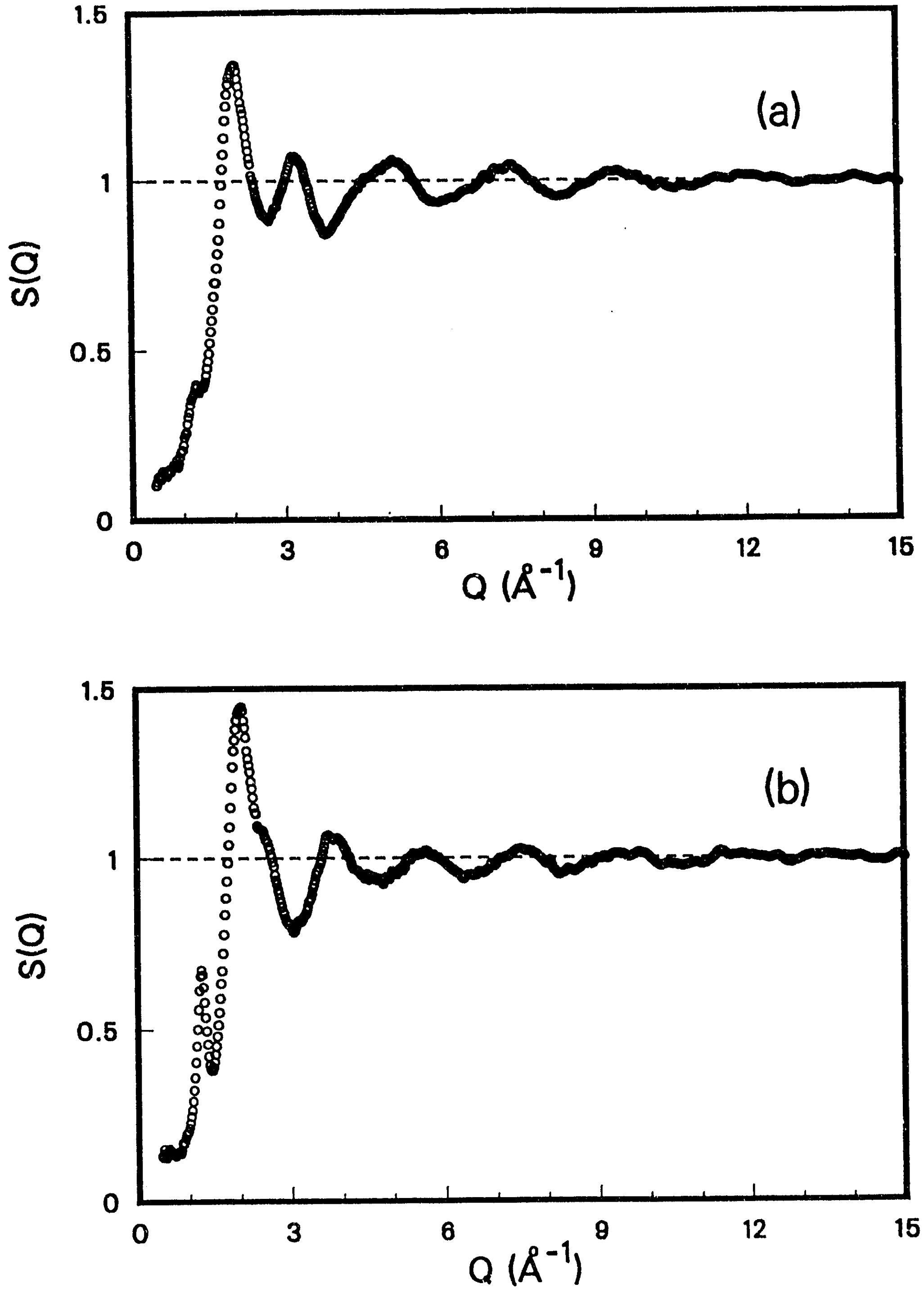
Fig 1. Saboungi et al



Saboungi et al
Fig 2



Dubourg et al Fig 3



Saboungi et al Fig 4

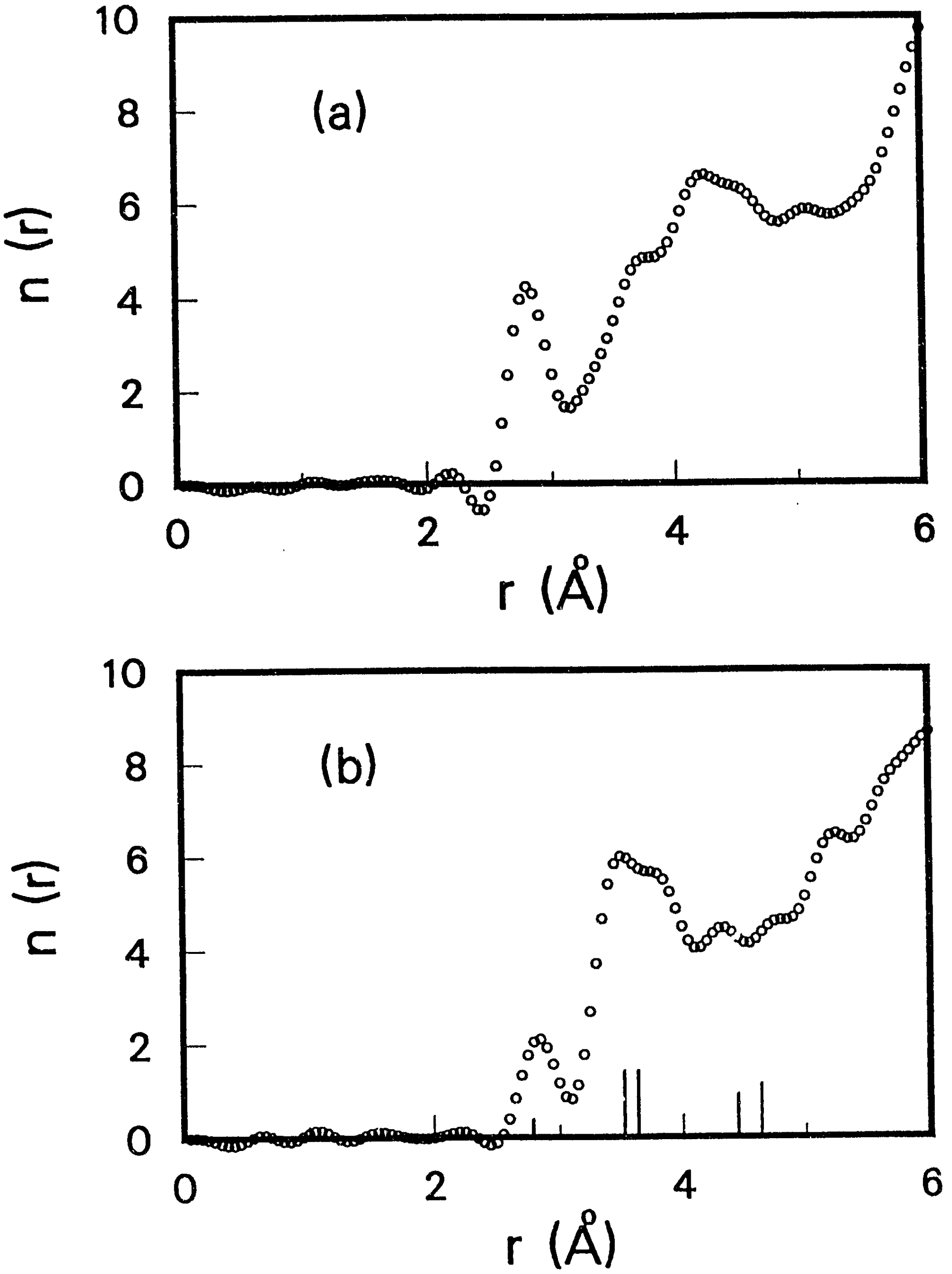


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Fig 5

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