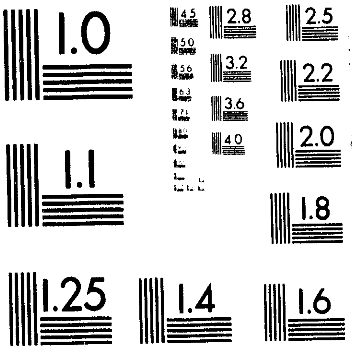
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1.4
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1 of 1

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Structural ordering in liquid K-Te alloys

J. Fortner, M.-L. Saboungi and J. E. Enderby *
Argonne National Laboratory, *Argonne*, *IL* 60439 (*USA*).

Abstract

Neutron diffraction from molten K_xTe_{1-x} is reported for x=0.12 and x=0.50 semiconducting alloys. The measured radial distribution functions (rdf) demonstrate the persistence of covalently bonded tellurium in the liquid. The rdf of the liquid $K_{0.12}Te_{0.88}$, which is dominated by the Te-Te contribution, is remarkably similar to that of pure liquid tellurium, the notable exception being that the nearest neighbor peak is largely resolved and found to have a coordination number slightly less than 2. The $K_{0.50}Te_{0.50}$ rdf clearly indicates Te-Te pairing in the melt, an unexpected departure from the presumed similar $Cu_{0.50}Te_{0.50}$. These paired tellurium are most likely of the form $(Te_2)^{2-}$ Zintl ions.

Introduction

Pure *l*-Te (where *l*- refers to liquid) has a coordination number that varies from ~2 to 3 with increasing temperature.[1,6] This coordination number appears to be closely related to changes in the electronic properties with temperature, such as conductivity and thermopower, from semi-metallic to metallic.[1], 7 − 9 In particular, the transition from semiconducting to semimetallic behavior upon melting has been attributed to the breaking up of the covalently bonded (2-fold) chains and the introduction of threefold coordinated sites.[1,7]. This interpretation is somewhat tentative, however, in part because the first coordination sphere of *l*-Te as determined by neutron scattering is not well defined due to penetration by non-bonded second neighbors.[1,6,9] This is in contrast to liquid selenium, where a well-defined first coordination peak with an area of 2 atoms has been observed[10] with neutron diffraction.

True liquid semiconductors, that is, liquid matter with $\sigma < 500\ \Omega^{-1}\mathrm{cm}^{-1}$ and $\delta\sigma/\delta T > 0$ where σ is the electrical conductivity, and T is the temperature, often occur in the form of binary alloys. In these systems, the unusual semiconducting properties are a direct consequence of local, or chemical ordering.[1,2]

Recent thermodynamic investigations of the potassium-tellurium system[3] have shown that for several compositions there is considerable "excess stability," indicative of chemical ordering. Of particular interest is the nature of this ordering at the approximate compositions $K_{0.12}Te_{0.88}$ and $K_{0.50}Te_{0.50}$ corresponding to local maxima in the excess stability function. Near the equiatomic composition, one expects an "ionic alloy" type of ordering due to the large electronegativity difference between K and Te.[1−4] Here, the "Zintl rule[5]" would suggest the formation of $(Te_2)^{2-}$ anions if the charge transfer from K to Te is complete. For

zb

compositions much less than 50% K, the tendency for Te to form covalently bonded chains, which are known to survive into the melt, will be significant.[1,5] Both of these compositions are true liquid semiconductors (as defined by Enderby and Barnes[1]), with $\delta\sigma/\delta T > 0$ and with conductivities of 200 and 1 $\Omega^{-1}\mathrm{cm}^{-1}$ for x =0.12 and x=0.50, respectively[6].

Experiment

Samples were prepared by direct synthesis of tellurium powder with potassium in a helium filled glovebox (< 100 ppb H_2O). The reaction of Te powder with the molten potassium is highly exothermic, and must be carried out very slowly by adding small (< 1mg) quantities of Te. The alumina crucible containing the partly reacted K-Te mixture was then sealed in a stainless steel vacuum nipple and annealed above the liquidus (~ 450 °C). The $K_{0.50}Te_{0.50}$ obtained was a dark purple crystalline material. Some of this was mixed with pure Te to produce the $K_{0.12}Te_{0.88}$.

The samples were then sealed under vacuum in thin walled (0.5 mm) fused silica ampoules, and one empty ampoule for container subtraction was prepared. 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 ~ 450 °C. Standard programs for intensity, background, absorption, multiple scattering, and inelastic scattering were run. The total structure factors, $S(Q)$, were obtained and Fourier transformed to obtain the total reduced radial distribution functions (rdf), $T(r)$ by

$$T(r) = 4\pi r\rho_0 + Q[S(Q) - 1] sinQr\ M(Q)dQ \qquad \text{(eq. 1)}$$

where ρ_0 is the average atomic density and $M(Q)$ is a damping function to reduce termination ripples in the Fourier transform. The measured total structure factors are shown in figures 1 and 2 for $K_{0.12}Te_{0.88}$ and $K_{0.50}Te_{0.50}$, respectively.

Note that the relative contributions of the partial structure factors (and consequently, via Fourier transform, the partial radial distribution functions) to the total measured structure factors are given by

$$S_{tot}(Q) = 0.847\ S_{Te-Te}(Q) + 0.007\ S_{K-K}(Q) + 0.146\ S_{K-Te}(Q) \qquad \text{(eq. 2)}$$

for $K_{0.12}Te_{0.88}$ and

$$S_{tot}(Q) = 0.375\ S_{Te-Te}(Q) + 0.152\ S_{K-K}(Q) + 0.473\ S_{K-Te}(Q) \qquad \text{(eq. 3)}$$

for $K_{0.50}Te_{0.50}$. In the former case, the K-K contribution is negligible and the K-Te contribution is small, whereas for the latter case each partial pair distribution is substantial.

In figure 3 the reduced rdf, $T(r)$, for the molten $K_{0.12}Te_{0.88}$ alloy is shown. Of significance here is the clear separation of the first peak in the rdf from the rest of the neighbors. A Gaussian fit to this first peak, at a distance of 2.8 Å and with an area of 1.7 atoms, indicates Te chains (about 5 atoms long) persisting into the melt. It is interesting to note, additionally, that otherwise the rdf is quite similar to that of pure liquid Te, suggesting 2-fold, rather than

3-fold bonding in the pure system. An additional peak at 3.6$\AA$, matching the sum of the K^+ and Te^{2-} ionic radii, is attributed to the K-Te first coordination sphere.

The role of the potassium appears to be that of nearly complete charge transfer to the Te clusters. The additional electrons stablize the short chains as $Te_n^{(2-)}$ ions. These charged chains in a dilute K^+ matrix will certainly interact much more weakly than the equivalent chains in the pure system, which is believed to contain a high density of 1F and 3F "defects." From this point of view, the first peak in rdf of pure l-Te may be viewed as containing a contribution from long-lived 2-fold (intra-chain) and short-lived threefold (3F) (inter-chain) and onefold (1F) (chain termination) sites. The 3F and 1F sites are in "fast exchange" as short chains interact. This view would be consistent with the rapid transition to semiconducting behavior with alloying Te with Se[8], Tl[1], or K[7]. Magana and Lannin[11] have also suggested that 3-fold bonding is needed to explain the Raman spectra of pure l-Te, and their observation of a sudden qualitative change in the Raman spectra of the Se-Te system at ~ 20-30 atomic percent Se was interpreted as a transition from 3-fold to 2-fold bonding. This is reasonable when one compares the time scales involved in Raman scattering (10^{-p} s) with neutron diffraction (10^{-q} s), keeping in mind that the 3F sites may dominate the Raman spectra yet appear obscured by fast exchange in the diffraction data. A recent EXAFS study[12] of $l-$Te has attributed the broad first coordination sphere to the presence of long (3.0 $\AA$) and short (2.8 $\AA$) bonds, though preserving 2-fold coordination. The two types of bond were attributed to the interaction of lone pair orbitals between chains.

The $T(r)$ for liquid $K_{0.50}Te_{0.50}$ (figure 4) shows that there is again a first Te-Te coordination peak at 2.8 $\AA$, 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).[13] It is informative to compare this liquid structure with that of crystalline KTe, [13,14] whose peaks are indicated by the vertical bars with numbers in parenthesis indicating coordination. 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 molten salts. The large, broad, and assymetric second peak at about 3.5 $\AA$ 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.

The unusual assymetric shape of the Te-K peak at 3.5 $\AA$ precluded any reasonable fitting with Gaussians. This shape is likely due to the K^+ ions arranging themselves about a "dumbell-shaped" $(Te_2)^{2-}$ polyion.[4,14,15] As the inter-ionic Te neighbors are so strongly correlated in position, the position of the K^+ will depend on an effective 3-body interraction, and the usual symmetric structure of the $T(r)$ peak will not be produced. The absence of ordering among the $(Te_2)^{2-}$ indicates effective screening by the K^+.

Conclusions

Neutron diffraction on molten $K_{0.12}Te_{0.88}$ and $K_{0.50}Te_{0.50}$ indicate varied structural ordering in these two liquid semiconducting alloys. Tellurium chains of varying length appear in this binary system, down to the diatomic $(Te_2)^{2-}$ Zintl ion. The existance of covalent bonding between tellurium ions has been observed under two vastly different conditions, suggesting the formation of variable-length 2-D Zintl ions.

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* Permanent address: H. H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL (UK).

References

1. J. E. Enderby and A. C. Barnes, Rep. Prog. Phys. 53, 85 (1990), and references therein.
2. M.-L. Saboungi, W. Geertsma, and D. L. Price, Annu. Rev. Phys. Chem. 41, 207 (1990).
3. A. Petric, A. D. Pelton, and M.-L. Saboungi, J. Chem. Phys. 89 (8) 5070 (1988).
4. A. Hartman, L. Poth, and K. G. Weil, Z. Phys. D 19,181 (1991).
5. E. Zintl, J. Goubeau, and W. Dullenkopf, Z. Phys. Chem. Abt. A154, 1 (1931).
6. A. Menelle, R. Bellissent, and A. M. Flank, Europhys. Lett. 4 (6) 705 (1987).
7. J. Fortner, M.-L. Saboungi, M. Doyle and J. E. Enderby, unpublished.
8. J. C. Perron, Adv. Phys. 16, 657 (1967).
9. M. E. Welland, M. Gay, and J. E. Enderby, *Physics of Disordered Systems*, ed. D. Adler et al. (New York: Plenum) p. 695 (1985).
10. K. Suzuki, Ber.Bunsenges. Phys. Chem. 80 689 (1976).
11. J. R. Magana and J. S. Lannin, Phys. Rev. Lett. 51 (26) 2398 (1983); J. R. Magana and J. S. Lannin, Phys. Rev. B 29 (10) 5663 (1984).
12. K. Tamura *etal.*, J. Phys. Condens. Matter 3, 7495 (1991).
13. A. C. Barnes and J. E. Enderby, Phil. Mag. B 58 (5) 497 (1988).
14. J. Fortner, J. W. Richardson, M.-L. Saboungi and J. E. Enderby, unpublished.
15. P. Boettcher, Angew. Chem. Int. Ed. Engl. 27, 759 (1988).

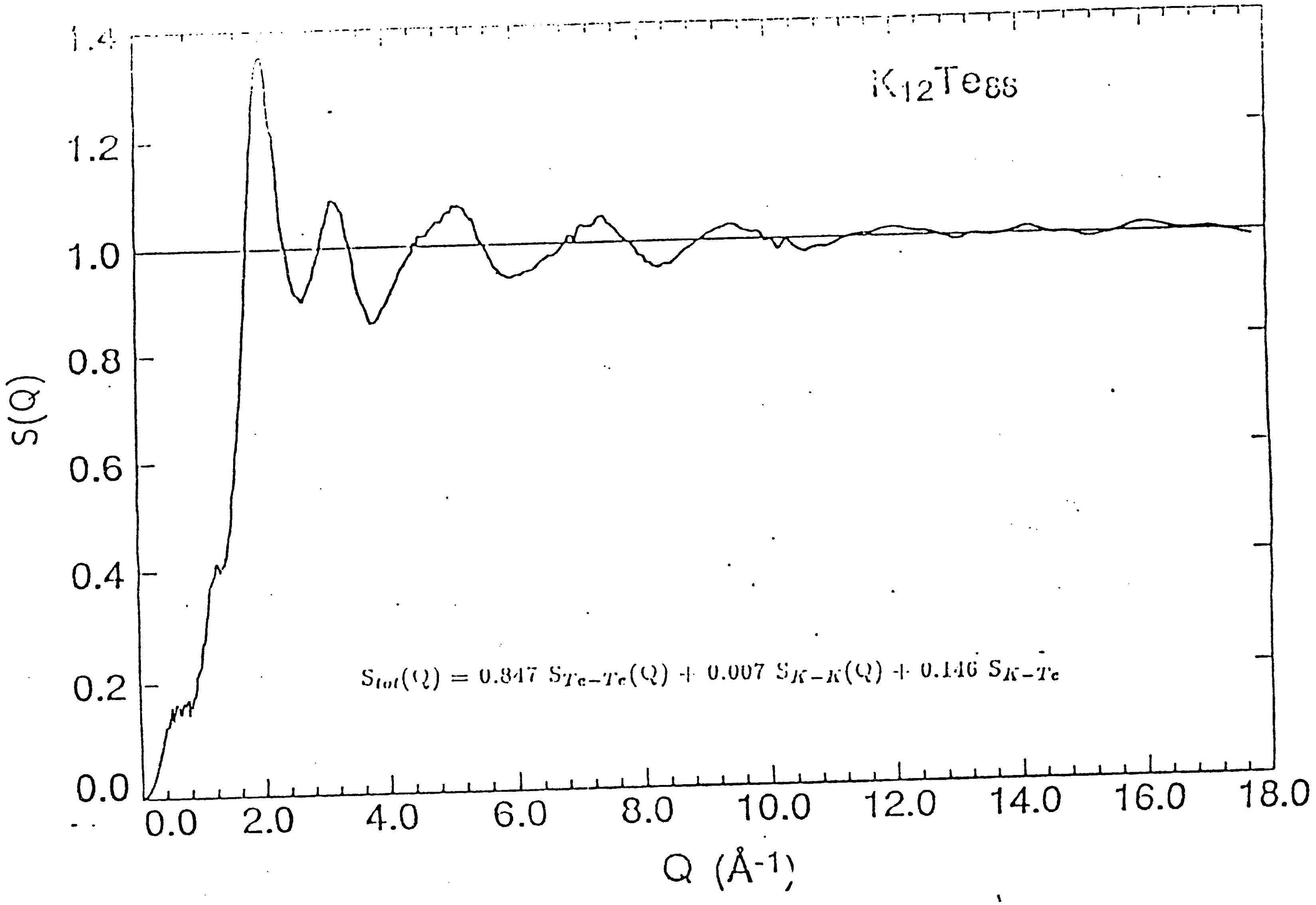
Figure Captions

Figure 1. The total structure factor for l–$K_{0.12}Te_{0.88}$ obtained by neutron diffraction.

Figure 2. The total structure factor for l–$K_{0.50}Te_{0.50}$ obtained by neutron diffraction.

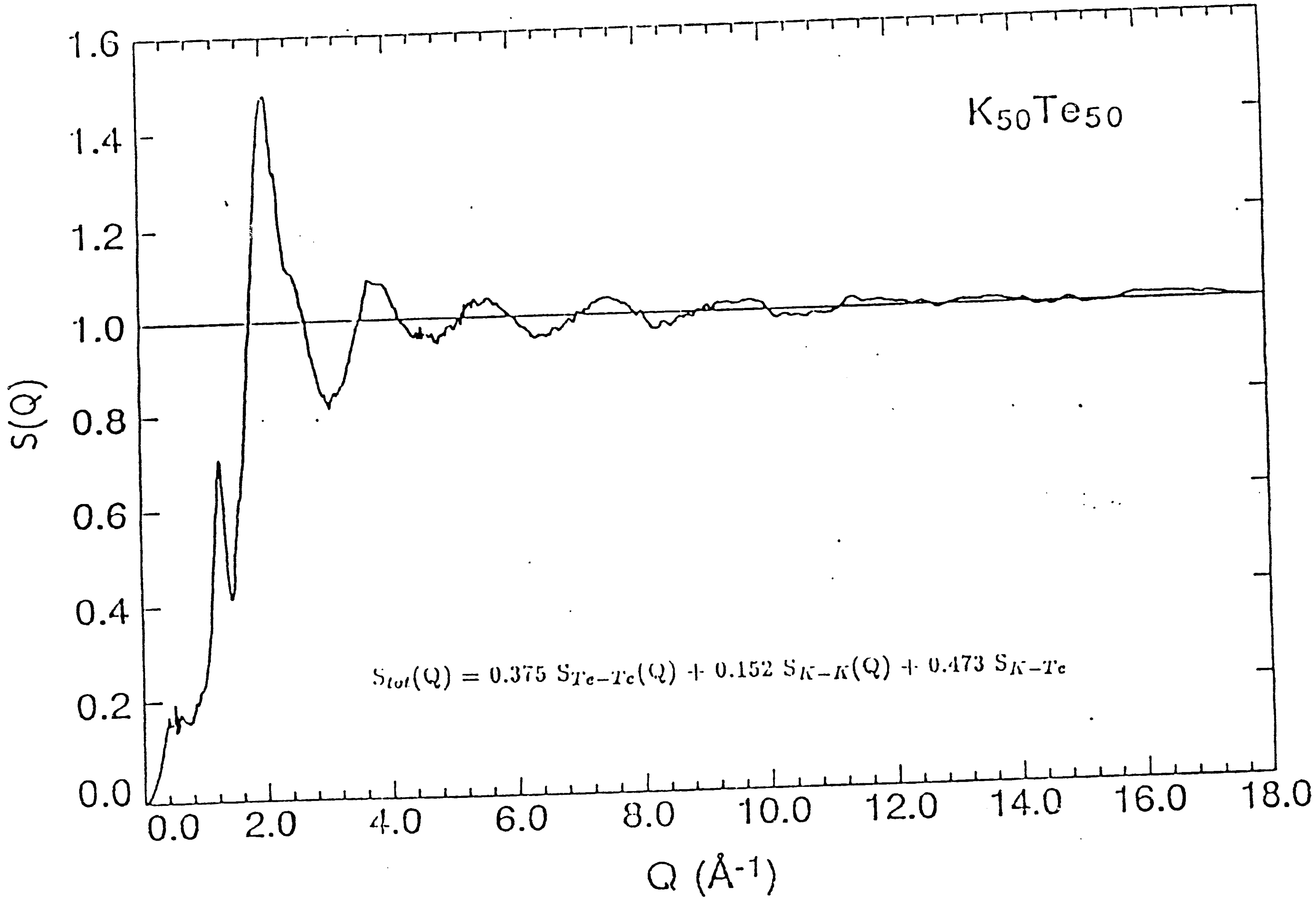
Figure 3. The total reduced radial distribution function for l–$K_{0.12}Te_{0.88}$ obtained from the data in Figure 1.

Figure 4. The total reduced radial distribution function for l–$K_{0.50}Te_{0.50}$ obtained from the data in Figure 2. The vertical bars represent the position of coordination shells in the crystalline phase from reference 14, with coordination numbers in parentheses.


K12Te88
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
S(Q)
$S_{tot}(Q) = 0.847\ S_{Te-Te}(Q) + 0.007\ S_{K-K}(Q) + 0.146\ S_{K-Te}$
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
Q (Å-1)

450°C

Fig. 1



$K_{50}Te_{50}$
$S_{tot}(Q) = 0.375\ S_{Te-Te}(Q) + 0.152\ S_{K-K}(Q) + 0.473\ S_{K-Te}$
S(Q)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
Q (Å^{-1})

F. 2

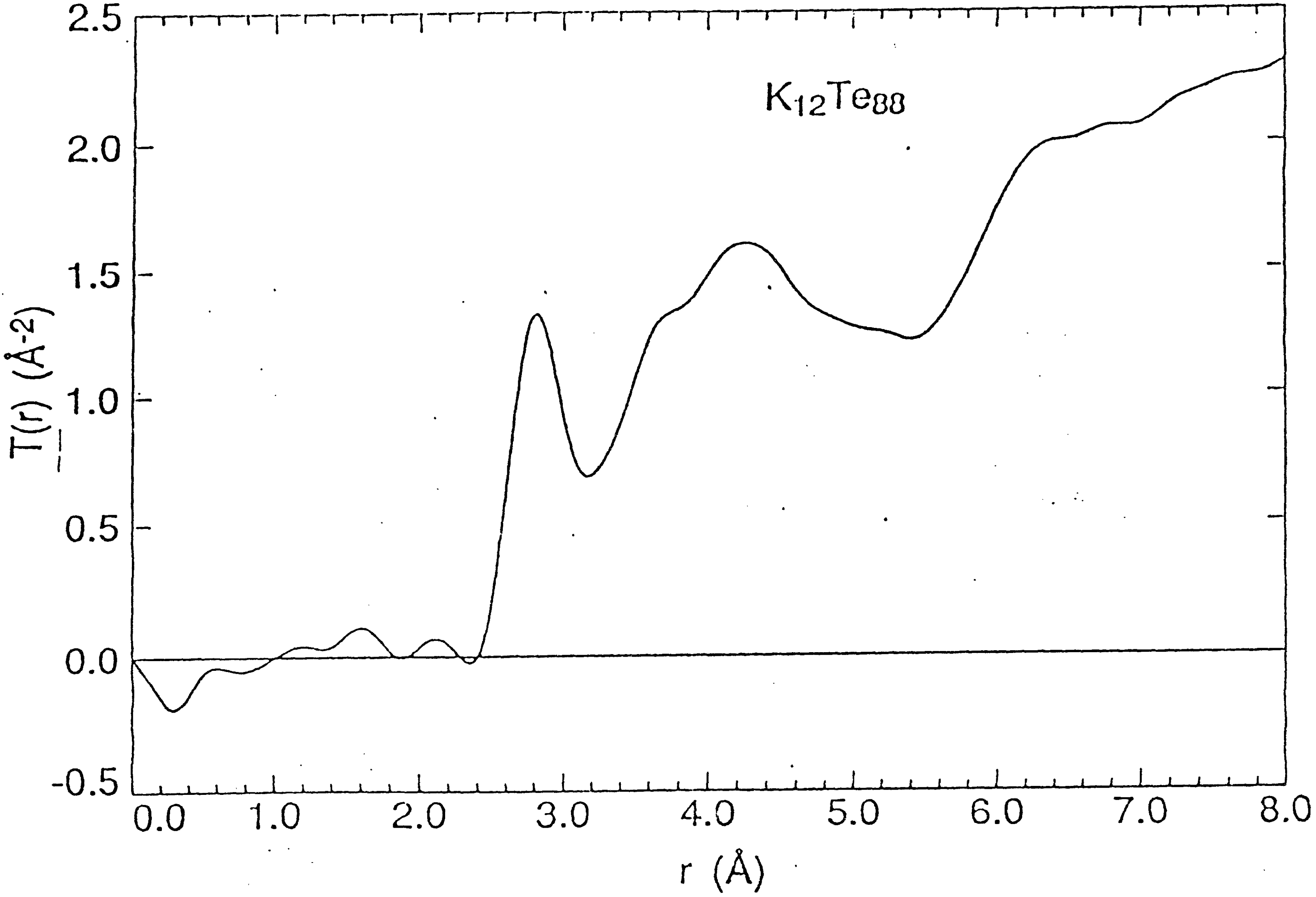


Fig 3

$\frac{n_1}{0.847} \times 0.38 = 1.7$ atoms ⟷ Te chains

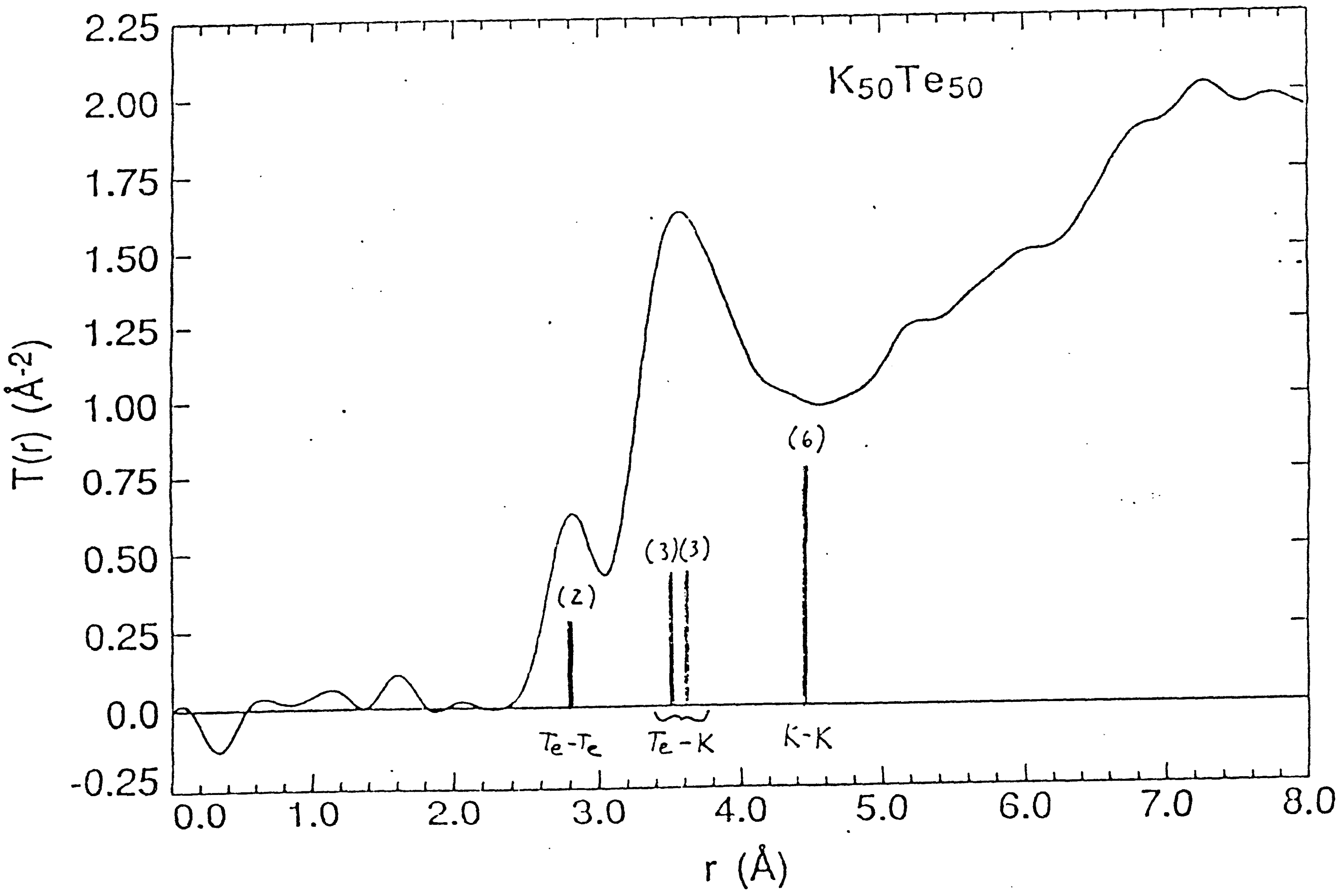


Fig 4

$\frac{n_1}{0.375} \times 0.50 = 0.95$ atoms ⟷ Te pairs

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