

## Nanometre superstructure in liquid alkali-thallium alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 9253

(<http://iopscience.iop.org/0953-8984/5/50/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 14:28

Please note that [terms and conditions apply](#).

## Nanometre superstructure in liquid alkali–thallium alloys

R Xu†, P Verkerk‡, W S Howells§, G A de Wijs†, F van der Horst†  
and W van der Lugt†

† Solid State Physics Laboratory, Materials Science Centre, University of Groningen,  
Nijenborgh 4, 9747 AG Groningen, The Netherlands

‡ Interfaculty Reactor Institute, Delft University of Technology, 2629 JB Delft, The  
Netherlands

§ Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX1 0QX, UK

Received 7 July 1993, in final form 11 October 1993

**Abstract.** Structure factors obtained from neutron diffraction measurements on liquid K–Tl and Cs–Tl alloys exhibit large prepeaks at approximately  $0.77 \text{ \AA}^{-1}$  and  $0.70 \text{ \AA}^{-1}$ , respectively. It is concluded that the liquid contains large units of thallium atoms, possibly bearing some resemblance to those found in crystalline  $\text{K}_3\text{Tl}_{11}$ .

### 1. Introduction

The work presented in this paper forms part of a systematic investigation of the properties of the liquid alloys of the alkali metals with post-transition group III metals. More particularly we refer to resistivity measurements on K–In [1], Rb–In and Cs–In [2, 3] and the liquid alkali–Tl alloys [4, 5]. They all exhibit the following pattern: firstly, for a given alkali metal the results are not strongly dependent on the group III element forming the second constituent of the alloy, and, secondly, in the sequence Li to Cs the maximum of the resistivity versus composition curve becomes higher, sharper and shifts to the equiatomic composition, where it is arrested for the K, Rb and Cs alloys as clearly shown in figure 1.

It was assumed that in the K, Rb and Cs alloys the resistivity peak is sufficiently high and sharp to be interpreted as an indication for compound formation at the equiatomic composition. This assumption is supported by density measurements in K–Tl alloys exhibiting a maximum in the volume contraction at 50 at% Tl [6]. Furthermore, optical measurements in Cs–Tl alloys show that an energy gap opens in the composition range between 40 and 50 at% Tl [7]. As a possible interpretation it was suggested that locally the structure might be similar to the  $B_{32}$  lattice, implying that fragmented  $\text{Zintl}$  ions would occur in the liquid (the perfect  $\text{Zintl}$  ion corresponding to a post-transition group III element has the configuration of the diamond lattice; it is realized in, for example, NaTl, LiAl and others).

There are several arguments in favour of this assumption: firstly, it would be in agreement with stoichiometry considerations; secondly, it would be in agreement with trends in the stability (size effects) of the solid compounds of Li and Na with Ga, In and Tl; and thirdly, an as yet unpublished reverse Monte Carlo analysis of neutron diffraction results on NaTl [8] by McGreevy provides indications for a local  $B_{32}$  configuration in the liquid.

A counter-argument is that there are no equiatomic solid compounds of In and Tl with the heavier alkali metals K, Rb and Cs, so the  $B_{32}$  structure is not realized in these systems.

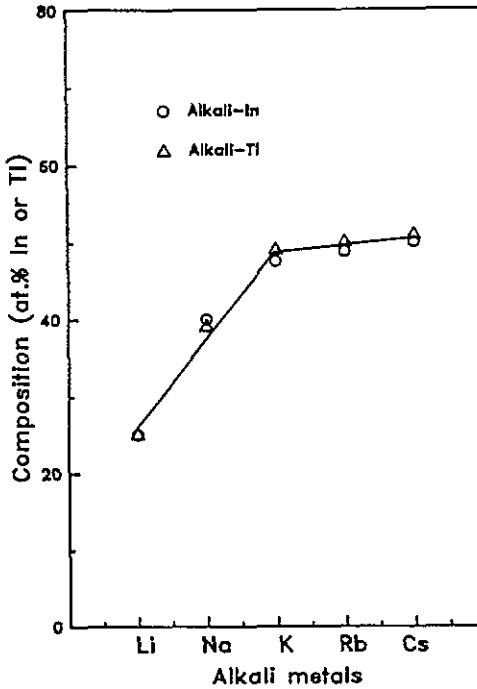


Figure 1. Compositions corresponding to the maximum resistivities for all alkali-In and alkali-Tl alloys.

As pointed out in [2] compact  $Tl_{11}$  clusters rather than network-like Tl configurations (as in the  $B_{32}$  lattice) occur in the solid compound  $K_8Tl_{11}$ , which is nearest to  $K_{0.5}Tl_{0.5}$ .

As the interpretation remained unsettled by lack of sufficient data, we decided to perform structural measurements on liquid K-Tl and Cs-Tl alloys. Tl alloys were chosen because In is not suitable for neutron diffraction because of its high absorption.

## 2. Experiments

The structure of five liquid alloys was obtained from neutron diffraction measurements with the time-of-flight diffractometer LAD, at the neutron spallation source ISIS, Rutherford Appleton Laboratory (RAL), UK. Some properties of the samples are summarized in table 1.

Table 1. Some properties of the A-Tl samples,  $\sigma_s$  is the total bound scattering cross section,  $\sigma_a$  is the absorption cross section at 1 Å,  $\sigma_{\alpha,\beta}$  are the cross sections for the partial (Faber-Ziman) structure factors, A stands for alkali metal K or Cs. Values of cross sections (in barn) are based on Sears [9].

Sample	$\sigma_s$	$\sigma_{A,A}$	$\sigma_{A,Tl}$	$\sigma_{Tl,Tl}$	$\sigma_a$
KTl	5.91	0.43	2.05	2.42	1.54
$K_3Tl$	3.94	0.97	1.53	0.60	1.35
$Cs_5Tl_7$	7.36	0.64	2.91	3.29	7.82
CsTl	6.87	0.92	2.99	2.42	9.01
$Cs_3Tl$	5.38	2.08	2.24	0.60	12.6

The cylindrical sample can consist of the zero alloy Ti-Zr with 0.5 mm wall thickness and 8 mm inner diameter. The standard RAL furnace and electronic control was used for keeping the K-Tl samples at  $350\text{ }^\circ\text{C} \pm 10\text{ }^\circ\text{C}$  and Cs-Tl samples at  $450\text{ }^\circ\text{C} \pm 15\text{ }^\circ\text{C}$ , which is well above the maximum temperature of the liquidus in the phase diagrams:  $335\text{ }^\circ\text{C}$  for K-Tl and  $428\text{ }^\circ\text{C}$  for Cs-Tl. The normal correction procedure [10] was applied, using a vanadium measurement for calibration, and empty-furnace and empty-can measurements for background correction. We were not (yet) able to produce fully corrected, physically meaningful, results for  $\text{Cs}_3\text{Tl}$ , probably because of the strong neutron absorption of that sample leading to highly wavelength-dependent attenuation factors in combination with the inaccurate (estimated) value of the density. The total structure factors  $S(q)$  for all the samples are defined by:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_s}{4\pi} + \frac{\sigma_c}{4\pi} [S(q) - 1]$$

where  $\sigma_c = 4\pi \langle b \rangle^2$  is the coherent scattering cross section of the sample, and  $\langle b \rangle$  is the average scattering length.

### 3. Results

The structure factors  $S(q)$ , except that for  $\text{Cs}_3\text{Tl}$ , are given in figures 2 and 3. We restrict the present discussion to the equiatomic compounds KTI and CsTI and for reasons to become clear below we will focus attention primarily on liquid KTI. The pair distribution function of liquid KTI, obtained by Fourier transforming the experimental  $S(q)$ , is shown in figure 4.

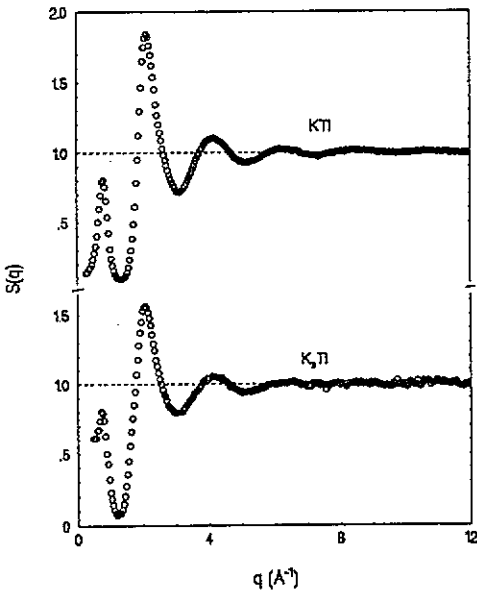


Figure 2. Total structure factors for liquid KTI and  $\text{K}_3\text{Tl}$ .

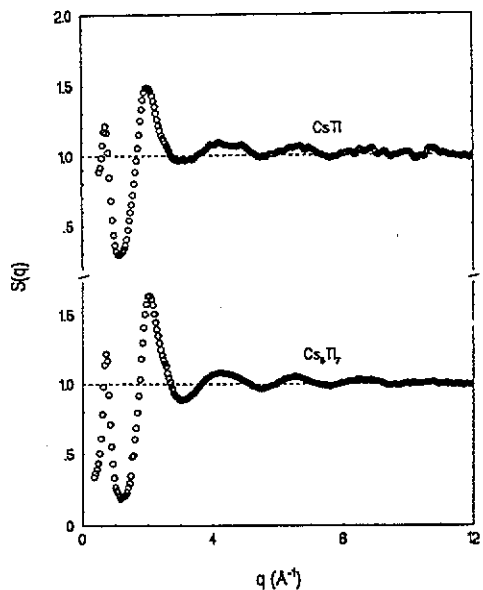


Figure 3. Total structure factors for liquid CsTI and  $\text{Cs}_5\text{Tl}_7$ .

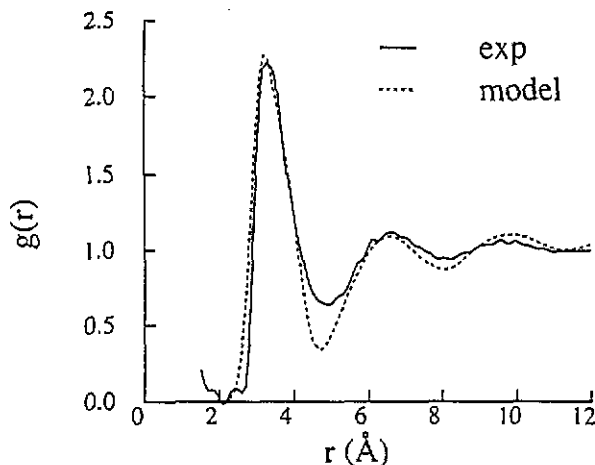


Figure 4. Calculated total pair distribution function of  $K_8Tl_{11}$  compared with that of liquid KTI alloy deduced from the structure factor by Fourier transformation.

The main feature of the structure factor is the prepeak. Its position is at  $0.77 \text{ \AA}^{-1}$  for KTI and  $0.70 \text{ \AA}^{-1}$  for CsTI, respectively. A prepeak (also called first sharp diffraction peak) with such a short wavevector implies a long-range superstructure and is often an indication for the existence of larger molecular units. A recent example is the case of liquid alkali-lead alloys where units  $(Pb_4)^{4-}$  or neutral units  $A_4Pb_4$  occur in the liquid [11, 12].

Presuming that some kind of clusters occurs in the liquid alloys, we have tried to translate the position of the prepeak,  $q_0$ , into a periodicity (or cluster-cluster distance),  $d$ , in real space. The value of the product  $dq_0$  can be guessed in several ways. Treating  $d$  as the interatomic distance in a diatomic molecule [13, 14] yields  $dq_0 = 7.7$ . A value based on hard-sphere packing is  $dq_0 = 5\pi/2$  [15]. These values are in rough agreement with the measurements on liquid KPb and CsPb if one considers  $d$  as an average intercluster distance between  $Pb_4$  units [11].

Using  $dq_0 = 7.7$  we arrive at an intercluster distance of  $10 \text{ \AA}$  in KTI and  $11 \text{ \AA}$  in CsTI. We carried out a final check by Fourier transforming the prepeak of KTI separately. This yields a broad hump with a maximum at  $9.3 \text{ \AA}$ , which is only 7% lower than the estimate made above.

This means that the superstructure found is very long-ranged for a liquid alloy. Price *et al* [15] have given a classification of the intermediate-range order in glasses and alloys in terms of the product  $q_0r_1$ ,  $r_1$  being the nearest-neighbour atom-atom distance. If  $r_1$  is put equal to the position of the first peak in the pair distribution function, this product is equal to 2.54 for KTI. This value corresponds to values listed for oxide, halide and chalcogenide glasses rather than alloys (the latter range from 2.70 to 3.99 in the table given in [15]). This demonstrates the special position of liquid K-Tl and Cs-Tl alloys and supports the assumption of some kind of clustering.

#### 4. Discussion

The present investigation almost coincided with the discovery of new and intriguing clustered structures in solid alkali-group III alloys by a number of crystal-chemistry research

groups. Some rather arbitrarily chosen review papers are given as [16–18]. Ga, In and Tl occur in an astonishing variety of isolated and linked polyhedra and other forms of clusters. We will try to relate the structure of liquid KTI to these crystal structures, restricting our attention to compounds containing isolated clusters, as intuitively we do not believe that the long-range structures corresponding to the linked clusters can survive in the liquid. The most interesting candidate then is  $K_8Tl_{11}$ , as its composition is nearest to the equiatomic liquid compound investigated (the corresponding solid Cs compound is not yet known). It has been described by Cordier and Müller [19] and, in more detail, by Blase *et al* [20] and, independently, by Sevov and Corbett [21, 22]. For comparison we have also considered an older paper on  $Na_2Tl$  [23] and more recent ones on  $Rb_2In_3$  [24, 25].  $Na_2Tl$  contains  $Tl_4$  tetrahedra for the same reasons as the alkali-lead alloys contain  $Pb_4$ .  $Rb_2In_3$  contains  $In_6$  octahedra on a body-centred lattice.

$K_8Tl_{11}$  contains  $Tl_{11}$  polyhedra in the form of capped, trigonal prisms (figure 5), which are distributed over a large unit cell (see figure 6). In the crystal, the closest distance of approach between two cluster centres is 9.99 Å. To calculate a sort of average intercluster distance, appropriate for the liquid but not corrected for thermal expansion, we may put the clusters on a fictitious FCC lattice, while keeping the number density equal to that of the original crystal. In this way we find an intercluster distance of 10.1 Å.

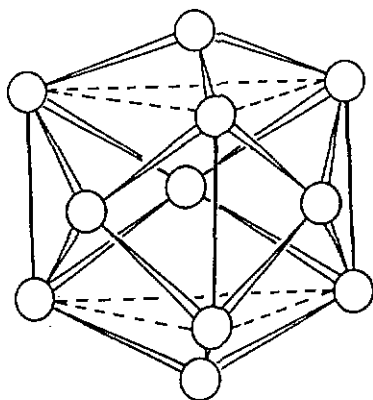


Figure 5.  $Tl_{11}$  cluster in  $K_8Tl_{11}$  compound.

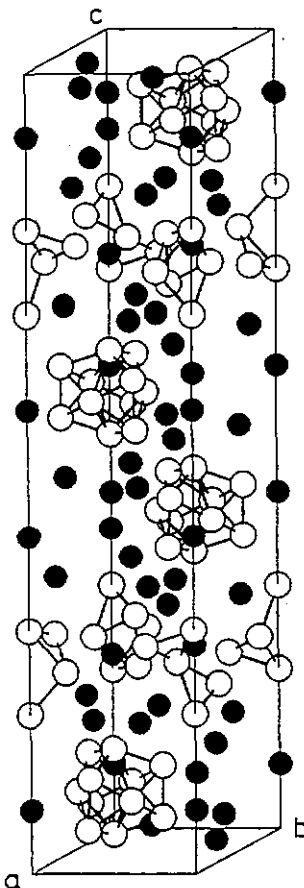


Figure 6. The unit cell of crystalline  $K_8Tl_{11}$ .

For comparison: the distance between the octaeders in  $\text{Rb}_2\text{In}_3$ , calculated by putting them on an FCC lattice, is 8.11 Å. Comparison of crystal structure determinations on K-In, Rb-In, K-Tl and Rb-Tl compounds [20] shows that the volume of the unit cell is remarkably insensitive to the particular combination of chemical elements. So the calculated distance of 8.11 Å is probably a fair approximation to the distance in the fictitious crystal  $\text{K}_2\text{Tl}_3$ . The distance between tetrahedra in  $\text{Na}_2\text{Tl}$ , calculated in the same way, is 7.98 Å. All these distances should be increased by a few (say 5) % to account for thermal expansion from room temperature to the melting point as well as through the melting point.

The average intercluster distance of crystalline  $\text{K}_8\text{Tl}_{11}$  comes close to the values estimated from the prepeak. As the composition of  $\text{K}_8\text{Tl}_{11}$  is also nearly that of the liquid investigated we have chosen this material for a more detailed comparison with the liquid.

An attempt was made to construct a pair distribution function from the structure of the crystal. This presumes an extreme similarity between the two phases which is not likely to exist in reality. Histograms of the distances in the solid were constructed for Tl-Tl, Tl-K and K-K pairs, normalized to obtain partial pair distribution functions  $g_{ij}(r)$  and convoluted with a Gaussian of variable width. Finally the partial pair distribution functions, weighted according to the neutron scattering lengths, were summed to obtain a total pair distribution function  $g(r)$  which can be compared with experiment. The width  $a$ , of the Gaussian,  $\exp(-r^2/a^2)$ , was chosen according to a prescription by Frenkel [26], where  $a^2 = 2Dr$ ,  $r$  is the pair distance considered and  $D$  was chosen to be  $0.013 \text{ \AA}^{-1}$  for  $r < 5 \text{ \AA}$ , and  $0.026 \text{ \AA}^{-1}$  for  $r > 5 \text{ \AA}$ . Furthermore, to account for thermal expansion a dilatation of 4% was applied to all pair distances except those which are shorter than 5 Å. The dilatation factor of 1.04 is chosen such as to minimize the phase differences in the long-distance oscillations between the experimental and model pair distribution functions. This factor is in good agreement with the difference between the densities of the liquid and solid phase. The number density of the liquid,  $0.023 \text{ \AA}^{-3}$ , follows from the density measurements of Matsuda *et al* [6]. The number density of the crystal is  $0.0259 \text{ \AA}^{-3}$  and is derived from the volume of the unit cell [19]. The first peak, corresponding mainly to nearest-neighbour Tl-Tl distances, appears to be less strongly affected by thermal expansion. This was also found for the Pb atoms in the tetrahedra in  $\text{CsPb}$ , for which a similar analysis was carried out [12], and could be due to relatively strong covalent bonds within such clusters. Given the crudeness of the model and the difference in composition between the crystal and the liquid, the agreement between the model  $g(r)$  and the experimental one is remarkably good, perhaps slightly fortuitously so (see figure 4).

Next,  $g(r)$  was converted to a structure factor  $S(q)$  with a cut-off radius on  $g(r)$  of 35 Å. Considering this large cut-off radius, the spurious oscillations in front of the prepeak are unexpectedly large and may be a consequence of the artificiality of the model. Again the agreement with experiment is satisfactory, although the prepeak of the model structure factor is considerably too high (figure 7). This, of course, reflects the long-range order existing in the solid.

This nice agreement does not necessarily imply that perfect  $\text{Tl}_{11}$  clusters are present in the liquid. A pair distribution function is related to pair distances only and can therefore be interpreted in many ways, so it is possible to imagine that other (clustered) configurations can exist which produce approximately the same pair distribution function and/or structure factor. The Tl-Tl, K-Tl and K-K distances do not vary appreciably from one crystalline compound to another and there is a great variety of clusters in the solid state, so one should be suspicious of any claims that a model is unique.

More particularly, dissociation of the aggregates must occur at high temperatures and most probably has already occurred near the melting point. This is suggested by analogy

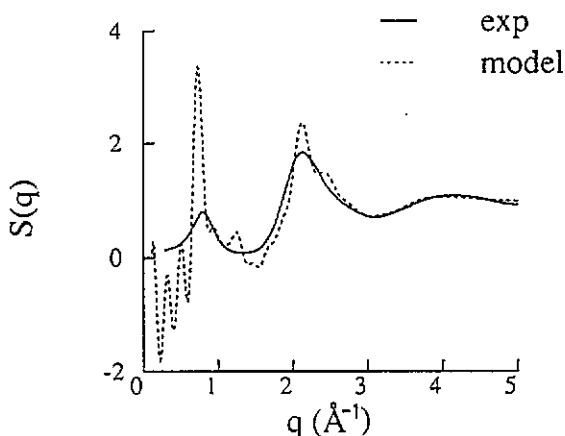


Figure 7. Calculated structure factor of  $K_8Tl_{11}$  compared with that of the liquid KTI alloy obtained from neutron diffraction experiments.

with the alkali-lead alloys, for which on the one hand the existence of clusters is evident from neutron diffraction measurements [11], but on the other hand their dissociation is an inevitable result from thermodynamic experiments [27].

The neutron diffraction data, and more particularly the prepeak, is in no way compatible with the original  $B_{32}$ -like model. The latter has to be given up in favour of a structural model containing large aggregates. The precise structure of these aggregates is still open to some speculation, but the model derived from crystalline  $K_8Tl_{11}$  is in quite reasonable agreement with experiment.

This leaves us with the problem of the difference between the compositions of the liquid and the solid compound. To solve this problem a deep insight in the quantum-chemistry of these compounds, also in the liquid state, is indispensable. As the electronic structure of solid  $K_8Tl_{11}$  is rather complicated [21], it is expected that this problem will not be solved in the immediate future.

### Acknowledgments

The authors cordially thank Dr G Cordier for promptly sending us yet unpublished results on  $K_8Tl_{11}$  and isomorphous materials, including a three-dimensional picture of the unit cell. They also acknowledge useful discussions with Professor J D Corbett and Dr J B van Tricht.

This work forms part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter (FOM)) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organisation for Scientific Research (NWO)).

### References

- [1] Meijer J A, Geertsma W and van der Lugt W 1985 *J. Phys. F: Met. Phys.* **15** 899
- [2] Xu R and van der Lugt W 1993 *J. Non-Cryst. Solids* **156/158** 289
- [3] van der Lugt W and Xu R 1991 *Int. Symp. Recent Developments in the Physics of Fluids (Oxford, UK)* ed W S Howells and A K Soper, F249



- [4] Kitajima M and Shimoji M 1976 *3rd Int. Conf. Liquid Metals (Inst. Phys. Conf. Series 30)* ed R Evans and D A Greenwood (Bristol: Institute of Physics) p 226
- [5] Itami T, Izumi K and Iwaoka R 1993 *J. Non-Cryst. Solids* **156/158** 285
- [6] Matsuda T, Nakamura Y, Kitajima M and Shimoji M 1977 *Ber. Bunsenges. Phys. Chem.* **81** 1182
- [7] Fainchtein R, Even U, Krohn C E and Thompson J C 1982 *J. Phys. F: Met. Phys.* **12** 633
- [8] Takeda S, Harada S, Tamaki S, Matsubara E and Waseda Y 1990 *J. Non-Cryst. Solids* **117/118** 68
- [9] Sears V F 1986 *Neutron Scattering (Methods of Experimental Physics 23)* Part A, ed L Skögl and D L Price (Orlando, FL: Academic) p 533
- [10] Soper A K, Howells W S and Hannon A C 1989 ATLAS—analysis of time-of-flight diffraction data from liquid and amorphous samples *Rutherford Appleton Laboratory Report RAL-89-046*
- [11] Reijers H T J, Saboungi M-L, Price D L, Richardson Jr J W, Volin K J and van der Lugt W 1989 *Phys. Rev. B* **40** 6018
- [12] Price D L, Saboungi M-L, de Wijs G A and van der Lugt W 1993 *J. Non-Cryst. Solids* **156/158** 34
- [13] Boos A, Steeb S and Godel D 1972 *Z. Naturf.* a **27** 271
- [14] James R W 1948 *The Optical Principles of the Diffraction of X-rays* (London: Bell)
- [15] Price D L, Moss S C, Reijers H T J, Saboungi M-L and Susman S 1988 *J. Phys. C: Solid State Phys.* **21** L1069
- [16] Belin C and Ling G 1983 *J. Solid State Chem.* **48** 40
- [17] Burdett J K and Canadell E 1990 *J. Am. Chem. Soc.* **112** 7207
- [18] Sevov S V and Corbett J D 1992 *Inorg. Chem.* **31** 1895
- [19] Cordier G and Müller V 1992 *Z. Kristallogr.* **198** 281
- [20] Blase W, Cordier G, Müller V, Häuslermann U, Nesper R and Somer M 1993 *Z. Naturf.* b **48** 754
- [21] Sevov S C and Corbett J D 1991 *Inorg. Chem.* **30** 4875
- [22] Sevov S C and Corbett J D 1992 *Chemtracts—Inorg. Chem.* **4** 55
- [23] Hansen D A and Smith J F 1967 *Acta Crystallogr.* **22** 836
- [24] Sevov S C and Corbett J D 1993 *Z. Anorg. Allg. Chem.* **619** 128
- [25] Cordier G and Müller V 1993 *Kristallographie* **203** 150
- [26] Frenkel J 1955 *Kinetic Theory of Liquids* (New York: Dover) p 113
- [27] Saboungi M-L, Reijers H T J, Blander M and Johnson G K 1988 *J. Chem. Phys.* **89** 5869