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1998 J. Phys.: Condens. Matter 10 3301

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The structure of molten alkali carbonates studied by neutron diffraction and *ab initio* calculations

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Received 1 December 1997, in final form 13 February 1998

Abstract. The total structure factors, $S(Q)$, of pure molten Li_2CO_3 and an equimolar mixture with K_2CO_3 , LiKCO_3 , were measured by neutron diffraction at 1013 K and 923 K, respectively. The results are generally consistent with the findings of previous MD simulations. The CO_3^{2-} ion remains essentially unperturbed in the mixture. The real-space pair correlation functions are consistent with a close-packed, regular, planar, trigonal geometry for the CO_3^{2-} ion in both Li_2CO_3 and LiKCO_3 . There is some indication, also consistent with the findings of MD simulation, of a possible tightening of the local coordination of CO_3^{2-} ions around Li^+ in the presence of the larger, more weakly polarizing K^+ cation. Modelling the $S(Q)$ data using structure factors calculated from monomer and dimer structures derived from *ab initio* quantum chemical calculations suggests that larger clusters are needed to realistically describe the melt local structure.

1. Introduction

Molten alkali carbonate mixtures show promise as electrolytes in fuel cells for the clean and efficient conversion of chemical into electrical energy. Because of the high operating temperatures and aggressive nature of carbonates, corrosion is a serious technical barrier to the commercial application of this technology. In studying the corrosion of various candidate electrode and container materials in Li_2CO_3 – K_2CO_3 melts, a strong dependence on composition was observed, which we believe is related to the details of the structure and dynamics in the melts [1]. In order to shed further light on the corrosion problem, we have undertaken an investigation of the structure of a pure molten carbonate and an equimolar mixture. The structures of pure Li_2CO_3 and K_2CO_3 melts have already been studied by x-ray diffraction, Raman spectroscopy, infrared spectroscopy and molecular dynamics (MD) simulations and the findings are summarized in an earlier paper [2]. Molten carbonate mixtures have been investigated using both x-ray diffraction [3, 4] and MD simulations [4, 5]. However, there still remain questions about the detailed structures of these melts. In particular, the MD simulations [5] suggest a tightening of the local coordination of CO_3^{2-} ions around Li^+ in the presence of the larger K^+ cation. However, this cannot be confirmed using x-rays because the technique is not sensitive to correlations involving light atoms such as lithium; hence the need for neutron diffraction measurements.

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In this paper, we present the results of neutron diffraction measurements on pure Li_2CO_3 and the equimolar binary mixture with K_2CO_3 , LiKCO_3 , as well as *ab initio* molecular orbital calculations for the Li_2CO_3 and LiKCO_3 dimers. The structure factors have been calculated using monomers and dimers and compared to the measured neutron $S(Q)$.

2. Methods

2.1. Neutron diffraction

The measurements were taken on the GLAD instrument at the Intense Pulsed Neutron Source, Argonne National Laboratory. Fully dried $^7\text{Li}_2\text{CO}_3$ (Tomiyama's High Purity Chemicals, 99.9%) and K_2CO_3 (Wako Pure Chemical Industries, Limited, 99.5%) were mixed and melted at 1073 K for pure Li_2CO_3 and 973 K for LiKCO_3 , respectively. The samples were allowed to cool under a dry nitrogen atmosphere, ground into powder and then dried for 90 minutes at just below their melting points. The powder samples were sealed under vacuum in platinum tubes of 0.1 mm wall thickness and 9.8 mm inner diameter. Measurements were carried out on pure Li_2CO_3 at 1013 K and the LiKCO_3 mixture at 923 K, as well as an empty platinum container of the same dimensions and at approximately the same temperature. For purposes of instrument calibration and data normalization, a vanadium standard and the empty instrument were also measured. The data were analysed and corrected for absorption, multiple scattering and inelasticity effects using standard procedures developed at Argonne for glass and liquid diffraction.

Table 1. Neutron scattering lengths, cross sections, and densities for alkali carbonate melts.

		^6Li	^7Li	C	O	K	Li_2CO_3	50 mol% Li_2CO_3 – 50 mol% K_2CO_3
$\langle b \rangle^a$	(fm)	2.00	−2.22	6.646	5.803	3.67	3.271	3.601
$4\pi \langle \bar{b}^2 \rangle^b$	(b)	0.970 00	1.400 00	5.551 00	4.232 00	1.96	3.508	4.252
$\langle \sigma_{abs} \rangle^c$	(b)	940.00	0.0454	0.0035	0.000 19	2.10	0.329	6.18
d^d	(g cm $^{-3}$)						1.827	1.94
ρ^e	(10 24 cm $^{-3}$)						0.0892	0.0661

^a Coherent scattering lengths.

^b Total scattering cross sections.

^c Absorption cross sections at 2200 m s $^{-1}$.

^d Mass densities (reference [6]).

^e Number densities.

The measured differential cross section per atom, $d\sigma_\alpha/d\Omega$, is related to $S(Q)$ by the equation

$$\frac{d\sigma}{d\Omega} = \langle \bar{b} \rangle^2 [S(Q) - 1] + \langle \bar{b}^2 \rangle \quad (1)$$

where

$$\langle \bar{b} \rangle = \sum_i x_i \bar{b}_i \quad (2)$$

and

$$\langle \bar{b}^2 \rangle = \sum_i x_i \bar{b}_i^2. \quad (3)$$

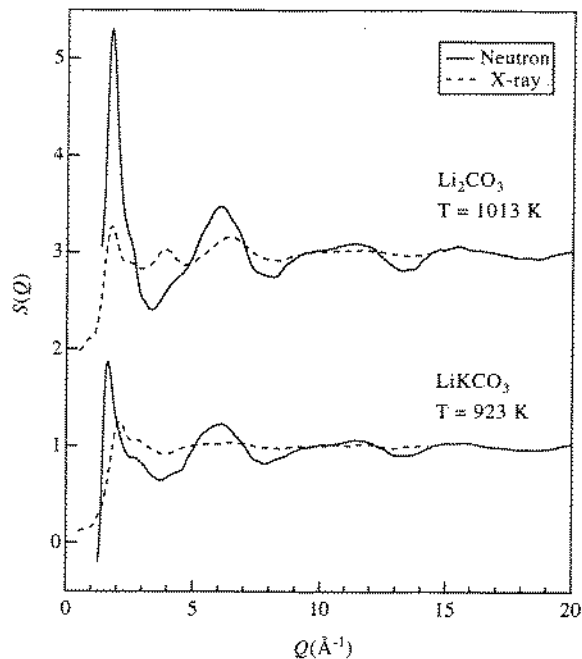


Figure 1. Measured structure factors $S(Q)$. The Li_2CO_3 data have been offset vertically by 2.

Here x_i denotes the concentration of the i th component and \bar{b}_i and $\overline{b_i^2}$ are the mean and the mean square scattering amplitudes, respectively, for component i averaged over the nuclear isotopes and spins for that component. In the case of a multicomponent system, $S(Q)$ can be regarded as the weighted sum of partial structure factors, $S_{ij}(Q)$, such that

$$S(Q) = \sum_{ij} x_i x_j \bar{b}_i \bar{b}_j \frac{S_{ij}(Q)}{\langle \bar{b} \rangle^2}. \quad (4)$$

The real-space differential correlation function, $D(r)$, is obtained from $S(Q)$ by taking the Fourier transform

$$D(r) = \frac{2}{\pi} \int_0^{Q_{\max}} Q [S(Q) - 1] \sin(Qr) dQ \quad (5)$$

and converted to the total correlation function, $T(r)$, using the relation

$$T(r) = D(r) + 4\pi\rho r \quad (6)$$

where Q_{\max} is the upper limit of the $S(Q)$ data and ρ is the number density. Neutron scattering lengths, cross sections, and densities for the samples are summarized in table 1.

2.2. *Ab initio* molecular orbital calculations and $S(Q)$

Since we had already calculated the geometries of various monomers for Li_2CO_3 and LiKCO_3 [2, 7], what remained in this study was to calculate the geometry of the dimers. As in earlier investigations [2], the calculations were carried out at the Hartree–Fock (HF) level employing the contracted Gaussian basis set 6-31G(*d*) and using GAUSSIAN 94 [8].

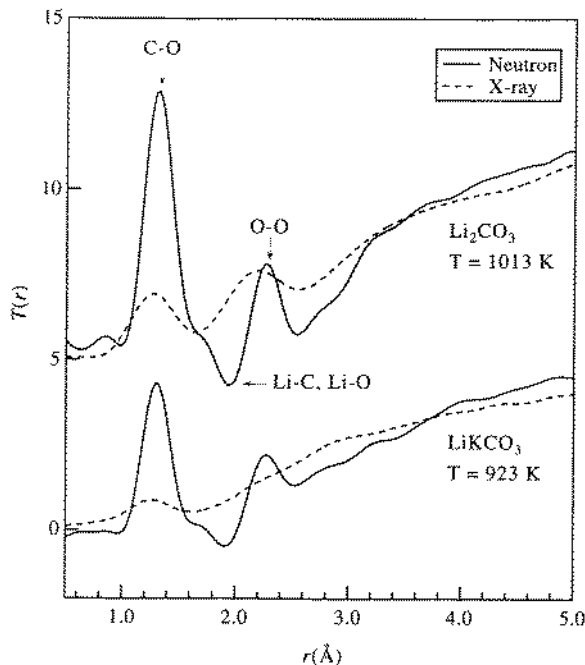


Figure 2. Measured total correlation functions $T(r)$. The pure Li_2CO_3 data have been offset vertically by 5.

Using the optimized geometries from the *ab initio* calculations, the model $S(Q)$ can be calculated using the Debye equation. If correlations between molecular orientations and positions can be neglected, $S(Q)$ takes the form

$$S(Q) = n\{f_1(Q) + f_2(Q)[S_c(Q) - 1]\} + 1 - \frac{\overline{\langle b^2 \rangle}}{\langle \bar{b} \rangle^2} \quad (7)$$

where $f_1(Q)$ is an intramolecular form factor and $f_2(Q)$ and $S_c(Q)$ are an intermolecular form factor and a molecular centre structure factor, respectively. The intramolecular form factor can be found from the following equation:

$$f_1(Q) = \frac{1}{n^2 \langle \bar{b} \rangle^2} \sum_i \sum_j \bar{b}_i \bar{b}_j \exp(-d_{ij} Q^2) \frac{\sin(Qr_{ij})}{Qr_{ij}} \quad (8)$$

where r_{ij} are the bond lengths and d_{ij} are the damping factors (taken from the values tabulated by Ohno [9] for the effects of thermal motion involving the atoms i and j). Applying the approximation $S_c(Q) = 1$, $S(Q)$ then becomes

$$S(Q) = \frac{1}{n \langle \bar{b} \rangle^2} \sum_i \sum_j \bar{b}_i \bar{b}_j \exp(-d_{ij} Q^2) \frac{\sin(Qr_{ij})}{Qr_{ij}} + 1 - \frac{\overline{\langle b^2 \rangle}}{\langle \bar{b} \rangle^2} \quad (9)$$

and thus can be readily calculated if the geometry of the molecules is known.

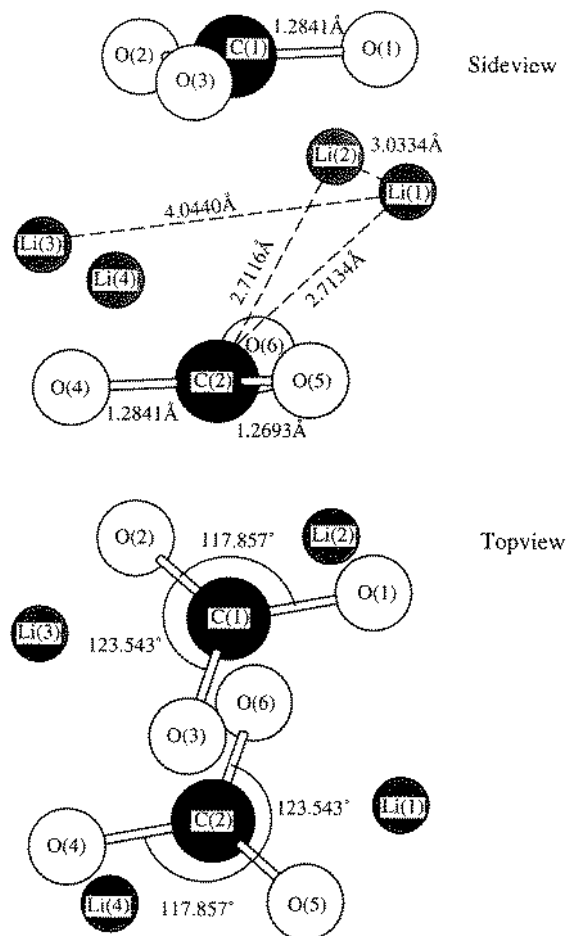


Figure 3. The optimized equilibrium structure for the Li_2CO_3 dimer calculated at the HF/6-31G(d) level.

3. Results and discussion

3.1. Neutron diffraction

The measured $S(Q)$ for molten Li_2CO_3 and LiKCO_3 binary mixture are shown in figure 1 along with the x-ray data of Ohno [9]. The neutron $S(Q)$ are more structured because of the stronger scattering from light elements, in particular lithium. They are also rather similar for $Q > 5 \text{ \AA}^{-1}$ where the intramolecular correlations of the CO_3^{2-} molecule are dominant, which suggests there is little change in the geometry of the ion. However, they do show differences at low Q , in the range $1\text{--}5 \text{ \AA}^{-1}$. In addition, the first main peak is at slightly lower Q in the mixture compared to the pure salt.

The real-space $T(r)$ functions for the pure carbonate and the mixture are shown in figure 2, again compared to the x-ray data of Ohno [9]. The features below $r \sim 1 \text{ \AA}$ are Fourier transform artefacts. For both salts, the first peak in $T(r)$, arising from the C–O correlation, is displaced from a position of approximately 1.31 \AA in the neutron measurement

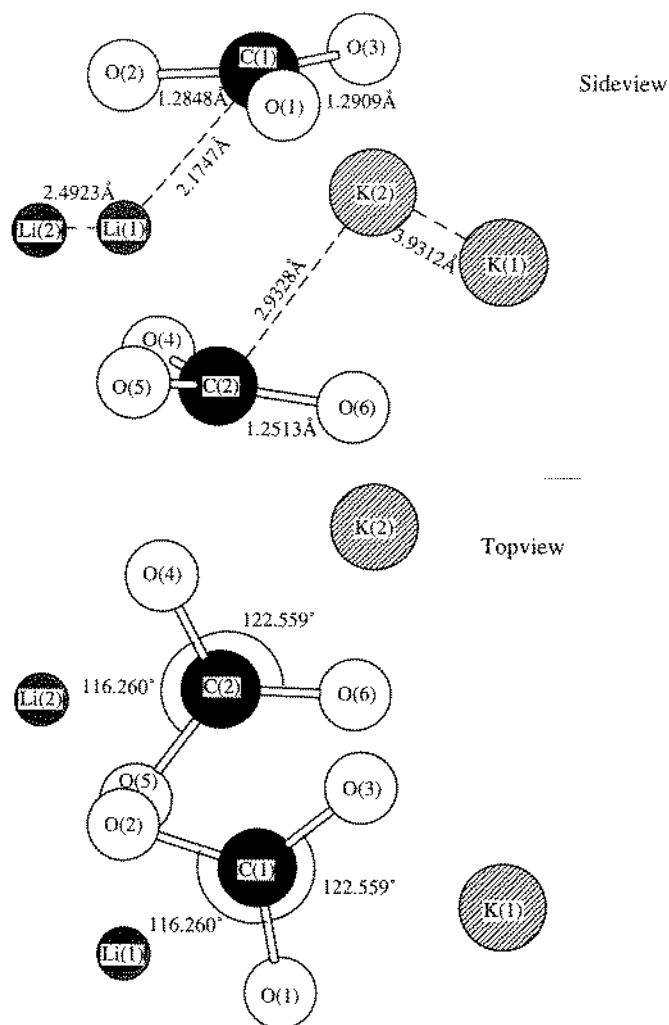


Figure 4. The optimized equilibrium structure for the LiKCO_3 dimer calculated at the HF/6-31G(d) level.

down to ~ 1.27 Å in the x-ray measurement. This displacement, along with noticeably higher intensity on the low- r side of the x-ray peaks, indicates a shift in electron density from the core positions and is consistent with strongly covalent bonding between C and O atoms in the CO_3^{2-} ion, as expected. The other marked difference between the neutron and x-ray data is seen immediately after the first main peak where the positive contributions from Li-O and Li-C correlations in the x-ray $T(r)$ contrast with the inverted peaks, arising from the negative scattering length of ^7Li , in the neutron $T(r)$. In the case of the mixture, peaks due to K-C and K-O correlations are expected in the range 2.5–3.0 Å but cannot be distinguished due to overlap with other peaks. The peak due to the O-O correlation is more readily identified in the neutron data than the x-ray data because of the stronger weighting and is seen to remain at approximately the same position, 2.26 Å, in both the pure salt and the mixture. Because there is also no change in the neutron C-O main peak position,

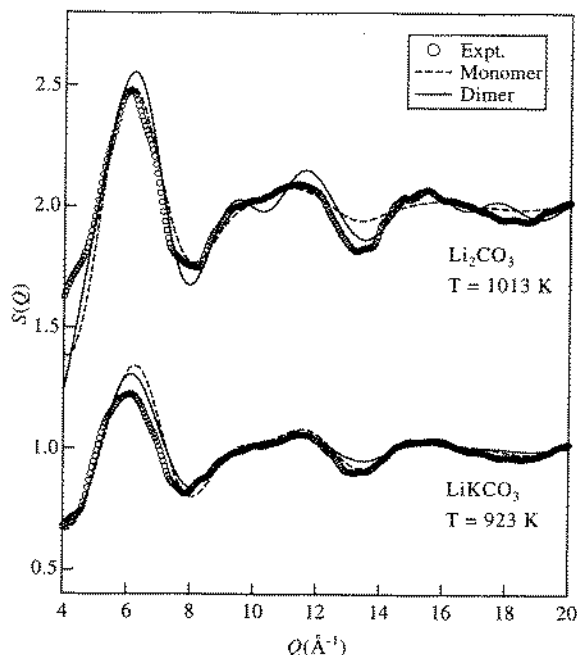


Figure 5. Measured and calculated structure factors. The pure Li_2CO_3 data have been offset vertically by 1.

the ratio of the O–O and C–O peak positions for both samples is ~ 1.725 , which agrees closely with the value of $\sqrt{3}$ (~ 1.732) expected for a close-packed, planar, regular trigonal CO_3^{2-} molecule. Again using the neutron data, the coordination number for O around C is estimated to have roughly the same value in both the pure salt and the mixture.

Also noticeable, going from the pure salt to the mixture, is a small but probably significant shift to lower r of the inverted peak due to Li–O and Li–C. It is appealing to consider this as being due to a tightening of the local coordination of CO_3^{2-} ions around Li^+ in the presence of larger, more weakly polarizing K^+ ions in the next-nearest-neighbour shell, which is consistent with the predictions of MD simulations [5].

3.2. *Ab initio* calculation

The equilibrium structures of the Li_2CO_3 and LiKCO_3 dimers are shown, with bond angles and distances, in figures 3 and 4, respectively. The optimized Li_2CO_3 dimer is made up of two CO_3^{2-} ions lying in planes parallel to each other, with the Li ions occupying sites in between. The geometry of the LiKCO_3 dimer is basically similar to that of the Li_2CO_3 dimer but slightly distorted due to the difference in size of Li and K. In addition, the bond lengths of the CO_3^{2-} ion in the LiKCO_3 dimer are slightly longer than those in the Li_2CO_3 dimer, again because of the larger alkali K.

3.3. Comparison of calculated and measured $S(Q)$

Total structure factors for Li_2CO_3 and LiKCO_3 monomers and dimers were calculated using structural parameters derived from *ab initio* calculation and the results are shown compared

against experiment in figure 5. While the main features are reasonably reproduced, the details are not. This suggests that larger clusters incorporating more CO_3^{2-} ions are needed for a realistic description of the local structure in these melts. Indeed, the MD results [5] indicate there are, on average, four CO_3^{2-} ions surrounding each alkali cation.

4. Conclusions

The total structure factors of molten Li_2CO_3 and LiKCO_3 have been measured by neutron diffraction at 1013 K and 923 K, respectively. The strongly covalent nature of the bonding in the CO_3^{2-} ion is indicated by the significantly lower C–O first peak position in the x-ray $T(r)$ compared to the neutron $T(r)$. The structure of the ion appears to be unperturbed in LiKCO_3 ; the C–O and O–O main peak positions remain the same as in pure Li_2CO_3 and are consistent with a close-packed, planar, regular trigonal geometry. Furthermore, the broad features of $S(Q)$ are rather similar for $Q > 5 \text{ \AA}^{-1}$ where the intramolecular correlations of the CO_3^{2-} ion predominate. The results are generally consistent with the findings of MD simulations [5] as regards the resilience of the CO_3^{2-} ion in the mixture. Also consistent with MD simulations is the noticeable shift to lower r of the inverted peak due to Li–O and Li–C correlations, suggesting a tightening of the local coordination of CO_3^{2-} ions around Li^+ in the presence of the larger, more weakly polarizing K^+ cation.

In addition, the neutron data have been modelled using structure factors calculated from hypothetical geometries, optimized by *ab initio* calculations, for Li_2CO_3 and LiKCO_3 monomers and dimers. The agreement with the $S(Q)$ data for dimers is encouraging and suggests that larger units are needed to realistically describe the structure of these melts. This conclusion would also appear to be in agreement with Tissen *et al* [5] showing that, on average, four CO_3^{2-} ions surround each alkali cation.

Acknowledgments

This work was supported by the US Department of Energy, Basic Energy Sciences, under contract No W-31-109-ENG-3. We thank the Operations Staff of the Intense Pulsed Neutron Source for making the measurements possible and also Dr K Takeuchi for assistance with the figures. The computations were carried out using the supercomputer NEC SX-3R at the Molecular Science Institute (Japan).

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