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1998 J. Phys.: Condens. Matter 10 525

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The structure of molten CuBr

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Received 17 April 1997, in final form 23 October 1997

Abstract. Reverse Monte Carlo modelling of isotopic substitution neutron diffraction data for molten CuBr (D Allen and R A Howe 1992 *J. Phys.: Condens. Matter* **4** 6029) is used to show that a flat partial radial distribution function $g_{\text{CuCu}}(r)$ is a possible numerical solution, but not a possible physical solution. The best model derived is a close-packed liquid of Br^- ions within which Cu^+ ions occupy approximately tetrahedral interstices. This structure is a natural continuation of trends as a function of temperature within the crystalline γ -phase and the fast-ion-conducting β - and α -phases.

1. Introduction

The structures of the molten copper halides have been studied and discussed for nearly 30 years. In one of the first neutron diffraction measurements using the technique of isotopic substitution to separate partial structure factors, $A_{ij}(Q)$, and hence derive partial radial distribution functions, $g_{ij}(r)$, Page and Mika [1] found evidence for a very flat (i.e. disordered) $g_{\text{CuCu}}(r)$, almost ‘gas-like’ in CuCl. Given that this result was rather different from the cation–cation correlations later found in similar studies of molten alkali halides [2–4], Eisenberg *et al* [5] repeated the measurement on CuCl and also derived a rather flat $g_{\text{CuCu}}(r)$, though slightly more structured than the earlier result. However, reverse Monte Carlo (RMC) modelling [6] of the data from [5] derived a definite first peak in $g_{\text{CuCu}}(r)$, comparable to that found for molten LiCl [7] (Li and Cu have similar ionic radii). In addition no computer simulation (see e.g. [8]) has yet been able to reproduce the flat $g_{\text{CuCu}}(r)$ derived in [1] and [5]. This seems to suggest that the flat $g_{\text{CuCu}}(r)$ is an artefact of the (very difficult) data analysis required to derive $g_{ij}(r)$. However, in a more recent experiment on molten CuBr, Allen and Howe [9] have derived a $g_{\text{CuCu}}(r)$ that is extremely flat, which then suggests that the RMC result may be wrong. In order to clarify the situation we have undertaken an RMC modelling study of molten CuBr. We show that a flat $g_{\text{CuCu}}(r)$ may be consistent with the experimental data in a numerical sense, but it cannot be reproduced by a physical structure and is therefore not ‘real’. It is probably caused by the use of a maximum-entropy method (which favours flat functions) to derive $g_{ij}(r)$ in [9]. Features of the RMC models for molten CuCl and CuBr are then discussed in relation to fast-ion (Cu) conduction in the crystalline phases.

2. MCGR derivation of $g_{ij}(r)$

The four experimentally measured structure factors [9], $F^{(k)}(Q)$ ($k = 1-4$), for molten CuBr are shown in figure 1. These are related to the partial structure factors, $A_{ij}(Q)$, by

$$F^{(k)}(Q) = \sum_{i,j} c_i c_j b_i^{(k)} b_j^{(k)} (A_{ij}(Q) - 1) \quad (1)$$

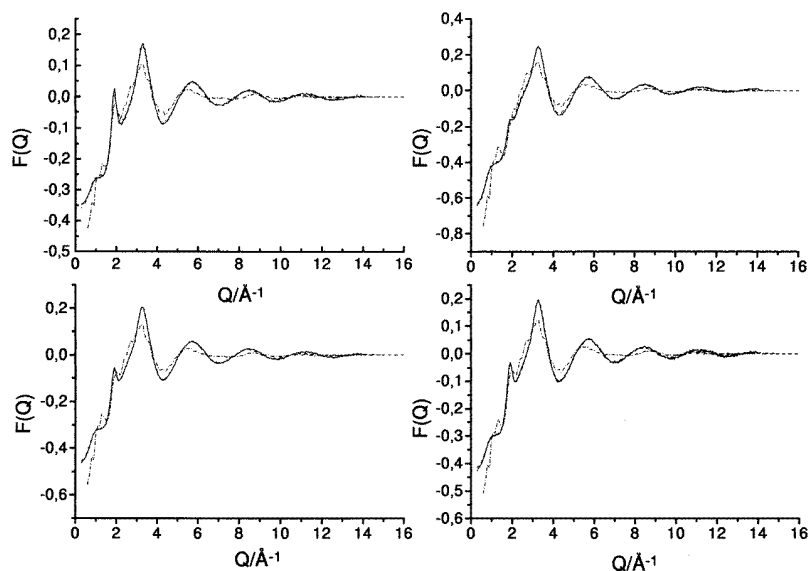


Figure 1. Total structure factors, $F^{(k)}(Q)$, for molten CuBr. Solid: experimental data [9]; dashed: MCGR fit; dotted: RMC model (i); chain: RMC model (iii). Top left: $^{100}\%^{63}\text{CuBr}$; top right: $^{100}\%^{65}\text{CuBr}$; bottom left: $^{50}\%^{63}+^{50}\%^{65}\text{CuBr}$; bottom right: $^{69}\%^{63}+^{31}\%^{65}\text{CuBr}$.

where $i, j = \text{Cu, Br}$, $c_i = 0.5$ is the concentration and $b_i^{(k)}$ is the coherent neutron scattering length for species i in sample k . In the present case only the scattering length for Cu varies between samples. The partial structure factors are related to the partial radial distribution functions by

$$A_{ij}(Q) = \rho \int 4\pi r^2 \frac{\sin Qr}{Qr} (g_{ij}(r) - 1) dr. \quad (2)$$

In a ‘conventional’ analysis the $A_{ij}(Q)$ are determined by solution of the simultaneous equations (1). (If the measurements are made for four samples the equations are over-determined since there are only three independent $A_{ij}(Q)$.) The $g_{ij}(r)$ are then determined from the direct Fourier transform (the inverse transform of equation (2)). Allen and Howe [9] used an inverse method to obtain $g_{ij}(r)$. A reference was not given, but the program is believed to be MCGOFR [10], in which the $g_{ij}(r)$ are generated numerically and modified by a Monte Carlo method in order to obtain good agreement between the calculated and measured $F^{(k)}(Q)$. At the same time a constraint was applied to maximize the entropy, defined as

$$H = -k \sum_{i=1}^N 4\pi r_i^2 g(r_i) (\ln(g(r_i)) - 1) \delta r \quad (3)$$

where N is the number of points in the $g(r)$ histogram and δr is the point spacing. k is a constant (a Lagrange multiplier). The effect of maximizing the entropy is to produce the ‘flattest’ $g_{ij}(r)$ which are consistent with the data. Note that this is not the same as the ‘smoothest’ since there are many possible definitions of ‘smooth’. This has been discussed in detail elsewhere [11].

We have derived $g_{ij}(r)$ using essentially the same method (the program MCGR [12]), but without the maximum-entropy constraint. An excellent fit to the data is achieved, as

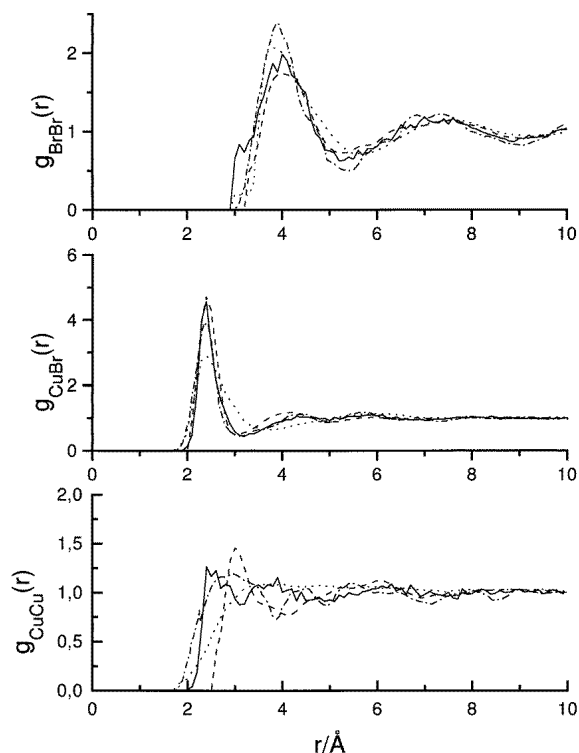


Figure 2. Partial radial distribution functions, $g_{ij}(r)$, for molten CuBr. Solid: RMC model (i); dashed: RMC model (ii); dotted: from [9]; chain: anomalous x-ray scattering results (from [17]).

shown in figure 1; the derived $g_{ij}(r)$ are shown in figure 2. $g_{\text{CuCu}}(r)$ is not flat, but rather has a distinct peak. This shows that a flat $g_{\text{CuCu}}(r)$ is only one possible *numerical* solution within the experimental errors; we show in the next section that it is not a possible *physical* solution.

3. RMC modelling

The RMC method has been described in detail elsewhere [13], in particular its application to studies of molten salts [6]. In the present work we have used models of 4000 ions in a cubic cell with periodic boundary conditions; all models were started from a random distribution. No experimental value exists for the density of molten CuBr. The value of 0.035 \AA^{-3} used by Allen and Howe [9] was considered to be rather low in relation to the known density of the crystal just before melting (0.041 \AA^{-3} [14]) and the density change of the related materials CuCl and AgI on melting. For this reason we have tested densities of 0.035 \AA^{-3} and 0.038 \AA^{-3} . This is found to make no significant difference to the results. (After completion of this work one of the referees drew our attention to an experimental value for the density of 0.0363 \AA^{-3} [15].) A number of different values of the allowed closest-approach distances of atoms have been tested. These are based on the direct solution for $g_{ij}(r)$ and information from studies of crystalline CuBr [14]. The values for Cu–Br and Br–Br were chosen as 1.9 and 2.9 Å respectively. Using lower values

produced no significant changes in the results. The Cu–Cu closest approach has been varied between 1.0 and 3.5 Å. Values larger than 2.1 Å resulted in a sharp ‘spike’ in $g_{\text{CuCu}}(r)$ at the cut-off distance. The spike disappeared for a closest approach less than 2.0 Å and decreasing the value further made no significant difference to the results, so this value has been used except in the case of the fit to $g_{ij}(r)$ derived by Allen and Howe [9] where a value of 1.8 Å, consistent with their result, has been used.

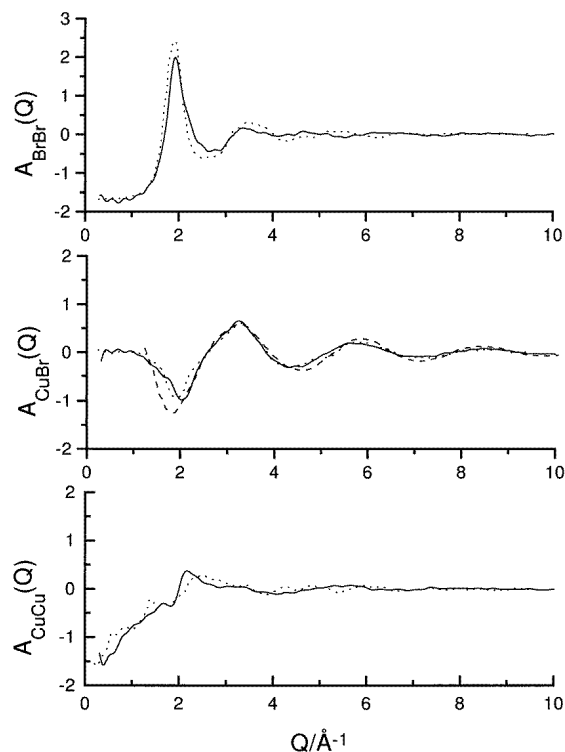


Figure 3. Partial structure factors, $A_{ij}(Q)$, for molten CuBr. Solid: RMC model (i); dashed: the EXAFS result (from [15]); dotted: anomalous x-ray scattering results (from [17]).

Three RMC models have been produced.

- (i) Fitting directly to the experimental $F^{(k)}(Q)$.
- (ii) Fitting to the $g_{ij}(r)$ derived by MCGR (section 2).
- (iii) Fitting to the $g_{ij}(r)$ derived by Allen and Howe [9].

The corresponding $F^{(k)}(Q)$ and $g_{ij}(r)$ are shown in figures 1 and 2 respectively. It was not possible to obtain a good fit in case (iii). The $F^{(k)}(Q)$ derived from the best fit $g_{ij}(r)$ in this case are significantly different from the experimental results. This indicates quite clearly that the Allen and Howe solution for $g_{ij}(r)$ [9] is a possible *numerical* solution, but not a possible *physical* solution. It was also not possible to obtain a very good fit in case (ii), though this was significantly better than case (iii). This indicates that the MCGR result is also not a possible physical solution. The main improvement comes from the increased height of the first peak in $g_{\text{CuBr}}(r)$, which is probably ‘over-flattened’ in the Allen and Howe solution by the maximum-entropy constraint [9].

We would suggest that the most reliable set of $g_{ij}(r)$ is that for case (i). Not only do

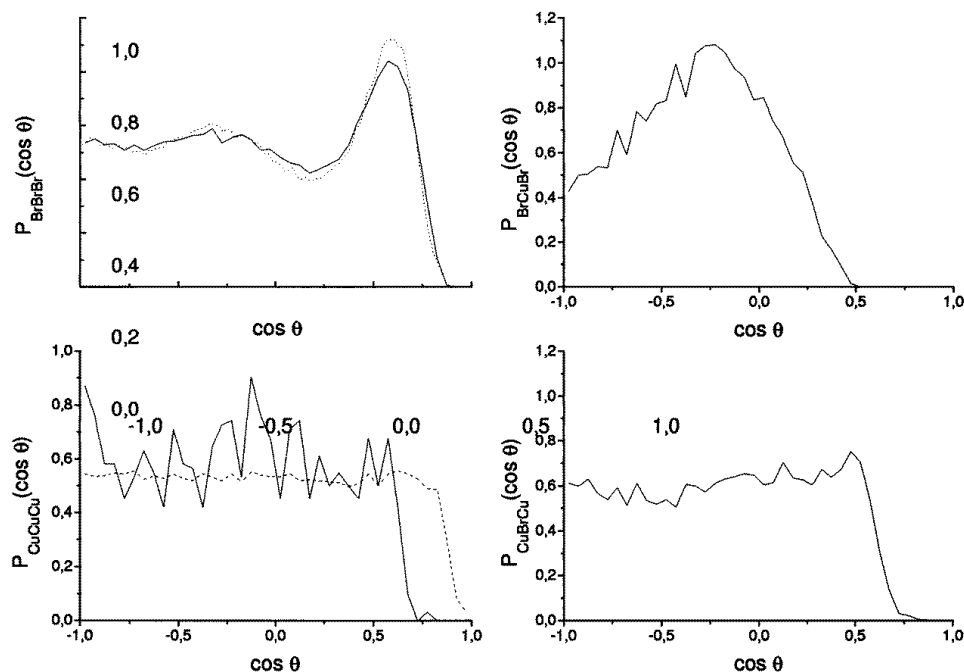


Figure 4. Angular correlations between near-neighbour atoms, $P_{ijk}(\cos \theta)$, for molten CuBr from RMC model (i). Br-Br neighbours are defined within 5.2 Å, Cu-Br within 3.3 Å and Cu-Cu within 5.1 Å (solid) and 3.2 Å (dashed). The results for P_{BrBrBr} are compared to those for molten Rb (dotted) [18].

they agree very well with the original data, but they also correspond to a physical model. However, we would stress that this is *not* a unique solution. There will be a number of sets of $g_{ij}(r)$ that satisfy the same criteria. Using a method that we have developed elsewhere for assessing the relative information content of different sets of isotopic substitution data [16] we find that the cosines of the angles between the characteristic vectors vary from 0.96 to 0.99. All of the values are very close to 1, which indicates that the four total structure factors have almost the same information content in terms of the partial structure factors. All of the RMC results for $g_{BrBr}(r)$ will therefore be very similar, those for $g_{CuBr}(r)$ will be slightly different, but there may be large variations in possible solutions for $g_{CuCu}(r)$.

Very recently an anomalous x-ray diffraction study of molten CuBr has been reported [17]. The partial radial distribution functions derived (also using RMC) are shown in figure 2. There is very good agreement for $g_{BrBr}(r)$ and $g_{CuBr}(r)$. The x-ray result for $g_{CuCu}(r)$ is intermediate between the RMC model (i) and MCGR results. In common with those results it shows definite structure and peaks at a significantly lower r -value than $g_{BrBr}(r)$. The cosines of the angles between the characteristic vectors for the x-ray data vary between 0.49 and 0.89, so the result for $g_{CuCu}(r)$ is in principle better than for the neutron data. However, in practice the x-ray data will contain larger systematic errors and hence the final errors in the two results are probably comparable.

The partial structure factors corresponding to RMC model (i) are shown in figure 3. A_{CuBr} is in good agreement with the results of a recent EXAFS study [18], except at the lowest Q (this is the region where EXAFS is least reliable). The $g_{CuBr}(r)$ derived from EXAFS has a significantly higher peak than the Allen and Howe result, and is also slightly

higher than the RMC model (i) result. This difference could be due to the fact that the EXAFS analysis has not considered any Cu–Cu contribution in the low- r region. Overall the differences are small enough that we are sure that both neutron diffraction and EXAFS data could be simultaneously fitted [19] without any significant changes to the RMC model (i). The partial structure factors from anomalous x-ray scattering [17] are also shown in figure 3. They agree well with the RMC model (i) results.

Figure 4 shows some of the angular correlations of near-neighbour atoms. P_{BrBrBr} has a shape typical of a close-packed simple liquid and is very similar to the result for molten Rb [20] (Br^- and Rb^+ are isoelectronic); the Br–Br coordination number is 11 (up to 5.1 Å). Within this structure the Cu preferentially occupy approximately tetrahedral interstices—the Cu–Br coordination is 3 (up to 3.3 Å) and P_{BrCuBr} peaks at $\approx 109^\circ$. There is very little angular correlation between neighbouring Cu atoms.

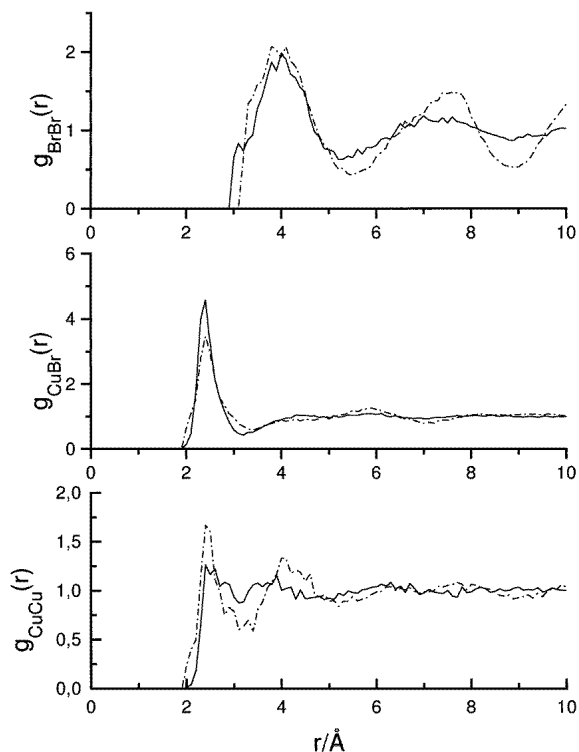


Figure 5. Partial radial distribution functions, $g_{ij}(r)$. Solid: molten CuBr, RMC model (i); chain: α -CuBr (from [14])

These results are consistent with studies of the crystal structure in the high-temperature, fast-ion-conducting α -phase [14]. Figure 5 shows $g_{ij}(r)$ for α -CuBr at 750 K. The first peak in g_{BrBr} is very similar but there is more long-range order in the crystal (as would be expected). The first peak in g_{CuBr} is lower than the RMC result for the liquid, but this may partly be due to the shorter Q -range of the crystalline measurement (giving lower real-space resolution). The coordination number in the crystal obtained by integrating up to the first minimum, as in the liquid, is also ≈ 3 , though from the crystal structure it is clear that the average coordination in a geometric sense is 4. This indicates that the coordination number obtained from a $g(r)$ should only be taken as an indication of the local environment.

$g_{\text{CuCu}}(r)$ has a definite first peak at 2.5 Å for both the crystal and the liquid, being lower in the liquid but with approximately the same area up to the first minimum. All of these features indicate that Cu ions have a similar local environment in the crystal and liquid; it is just slightly more disordered in the latter, as would be expected.

4. Discussion

For most isotopic substitution studies that are carried out in order to derive the partial radial distribution functions for a disordered system, the coefficient matrix is badly conditioned—in fact in most cases it is very badly conditioned. This means that there will be a wide range of possible numerical solutions for $g_{ij}(r)$ that agree equally well with the experimental data. The only *unique* solution is that obtained by direct matrix inversion of the original data and then direct Fourier transformation of the partial structure factors obtained (even this depends on the particular prior corrections that have been made to the data). However, this solution is very unlikely to be ‘correct’ since it will almost certainly involve finite values of $g_{ij}(r)$ at low r , i.e. atoms being closer than they can physically be. Simply removing this low- r part does not produce the correct solution either, since the systematic errors that produce these low r -values will also propagate to higher r . In addition there are almost certainly truncation errors due to the finite Q -range. These can be ‘modified’, but not removed, by multiplying $F^{(k)}(Q)$ by an appropriate modification function [21].

Inverse methods, like the MCGR program used here, offer another route to possible solutions for $g_{ij}(r)$ which can include ‘physical’ constraints such as requiring $g_{ij}(r)$ to be zero at small r . (Note that this is not the same as obtaining $g_{ij}(r)$ that are non-zero at low r and then removing the low- r part.) The use of maximum entropy as an additional constraint will produce the ‘flattest’ $g_{ij}(r)$ that are consistent with $F^{(k)}(Q)$. However, there is no physical or statistical reason to believe that this is a preferable solution. Certainly $g_{ij}(r)$ should be smoothed in some way to dampen statistical fluctuations which arise purely as a result of the Monte Carlo method, but there are many possible methods of smoothing. It should be noted that here it is the entropy of the derived functions $g_{ij}(r)$ that is maximized, whereas a more ‘normal’ use would be to maximize the entropy of the function(s) that are fitted to the data set itself, i.e. $F^{(k)}(Q)$. In addition the definition of entropy (equation (3)) is a ‘modified’ definition (normally $H = -p \ln p$), required because $g(r)$ is not a probability function (it does not have a definite integral). We would therefore suggest that maximum entropy, although it produces ‘nice-looking’ $g_{ij}(r)$, is neither mathematically or physically appropriate in this situation. It is more important that a solution for $g_{ij}(r)$ be physically sensible and probably the simplest way of doing this is by RMC modelling.

With regard to CuBr we have shown that a flat $g_{\text{CuCu}}(r)$ is not a physically sensible solution; the same applies for CuCl [6]. While a ‘flat’ result is appealing in a simple sense because it provides an obvious link to the high cation conductivity in the corresponding high-temperature crystals, it is now clear that such simplicity is misleading. Recent work has shown that fast-ion conduction in the crystalline phases is not a simple process [22], and there is no reason to suppose that it is in the liquid either. The influence of three-body forces may mean that the situation in the molten Cu halides is in fact more complex than in molten salts such as NaCl, where two-body forces alone provide a good description. For this reason the results shown here are not in better agreement with existing simulations (e.g. [8]) than the results in [9], since the simulations have so far only used two-body potentials.

One other point should be commented on. In a fast-(cat)ion-conducting phase a high degree of cation penetration into the first cation–anion coordination shell is to be expected, since this distance corresponds to ‘lattice site–interstitial’ distances; there must be some

degree of simultaneous occupation of lattice and interstitial sites if the material is conducting and cations do not all diffuse coherently (or at infinite velocity). This effect will probably persist into the liquid. It necessarily leads to a reduction in the height of the 'normal' first peak height of $g_{\text{cation-cation}}$ (i.e. that at the same distance as $g_{\text{anion-anion}}$). The fact that liquids which melt from fast-ion-conducting crystals show such an effect must therefore be considered as almost inevitable. What is notable from RMC results for crystalline and molten/crystalline AgBr, AgI, CuCl, CuBr and CuI [6, 14, 23–25] is that this penetration results in a distinct peak at low r (i.e. lower than that in the equivalent anion–anion partial), indicating that this short cation–cation distance is a significant feature of the structure. The peak intensity correlates well with the ionic conductivity, as should be expected from the argument given above. If RMC models are constrained to attempt to remove the peak then fits to the data are significantly worse. In a two-body approximation the only way to produce such a peak, while retaining charge balance, might be to reduce the effective charge to an extremely small value which would be considered unrealistic. Recent work by Wilson *et al* [26] suggests that three-body polarization effects may also be important, and in CuBr these may include polarization of both anions and cations.

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