I. INTRODUCTION

Structural and dynamical properties of solid and liquid ionic conductors have been investigated using various experimental and theoretical approaches. Simple binary superionic conductors such as silver and copper halides show several structural phase transitions at high temperature, associated with rapid changes of their conductivity. The increase in conductivity is due to the higher mobility of the ions at higher temperatures. Limiting ourselves to the subject of the present study, CuBr, there are several experimental investigations about crystalline structure, anharmonicity, and disorder effects using neutron diffraction and x-ray-absorption spectroscopy in the various high-temperature phases. Significant anharmonic effects related to the cation motion have been found using both techniques. Considerable efforts have been also devoted to the study of liquid copper halides. Neutron diffraction experiments of liquid CuCl and CuBr have given featureless Cu-Br pair distribution functions while halide-halide and Cu-halide distributions have been found essentially of ionic character. Very recent anomalous x-ray-scattering measurements of molten CuBr essentially confirmed previous neutron diffraction data. Computer simulations using not purely ionic interaction models have been also used to study such ‘superionic liquids’ although complete theoretical explanation of their peculiar behavior has not been yet found.

In this paper, we present a detailed XAS study of solid and liquid CuBr as a function of temperature, using an advanced multiple-edge EXAFS refinement in the framework of the multiple-scattering GNXAS method for data analysis. In solid CuBr we find an increasing asymmetry of the first-neighbor $g_{CuBr}(r)$ distribution function as a function of temperature. The foot and the most probable value of the first-neighbor distribution are found to shift up to about 0.09 Å toward shorter distances from 295 to 670 K, while the long-range part of distribution broadens at high temperatures. Results are discussed taking into account previous neutron diffraction and EXAFS results. A complete account of our EXAFS experiment on liquid CuBr is also reported. The short-range Cu-Br distribution is extracted showing evidence for nearly covalent bonding and improving previous neutron diffraction results. The short-range CuBr liquid structure is found to be quite similar to that of the high-temperature solid. The excellent short-range EXAFS sensitivity and its complementarity with usual diffraction techniques for studying disordered systems are discussed.

II. EXPERIMENTAL DETAILS

The CuBr samples were prepared starting from high-purity powder (99.999%, Aldrich chemicals). The powder was finely ground in a mortar and manipulated in a dry box. The resulting fine powder was mixed with graphite and pressed ($P \approx 7$ kbar) into pellets (thickness $\approx 1$ mm). Samples resulted to be a homogenous mixture of CuBr isolated micrometric particles into the inert matrix (graphite). This is a quite standard procedure to obtain samples suitable for high-temperature EXAFS (extended x-ray-absorption fine-structure) measurements. Pellets were stored under vacuum into glass ampules and protected from light before performing x-ray-absorption measurements. Verification of the optimal thickness of the samples was performed using a Rigaku laboratory EXAFS apparatus available at the Centro...
The Cu K-edge and Br K-edge EXAFS spectra were measured in transmission mode on beamlines D42-EXAFS 1 equipped with a channel-cut Si (331) monochromator and D44-EXAFS 4 equipped with a double-crystal Si (311) monochromator of the Laboratoire pour l’Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France). Low-noise EXAFS spectra were recorded at the temperature of 295, 400, 600, 670, and 793 K. XAS measurements as a function of temperature were performed using a high-temperature setup operating in vacuum and previously used for liquid metals and molten salts.\(^{19-22}\) The measured EXAFS spectra are characterized by a high signal-to-noise (S/N) ratio of $\sim 10^5$ for the Cu K edge and $\sim 10^4$ for the Br K edge.

As is well known, CuBr shows two solid-solid phase transitions characterized by a constant increase of the dc conductivity approaching its superionic $\alpha$ phase. We followed the structural variations in CuBr, recording several XANES (x-ray-absorption near edge structure) spectra.

In Fig. 1 we show some of the XANES spectra (left panel) along with their first derivatives (right panel), recorded as a function of temperature. The $\gamma \rightarrow \beta$ transition ($T = 658$ K) is clearly revealed both in the absorption and in the derivative spectra (see Fig. 1) by the decrease of the height of the main absorption peak around 8984 eV and by the disappearance of the small feature around 8990 eV. The $\beta \rightarrow \alpha$ transition ($T = 742$ K) is also monitored by the almost complete smoothening of the signal above the main absorption peak. The $\alpha$—liquid transition is marked by the softening of the main absorption peak. We notice that near-edge spectra of liquid and high-temperature solid CuBr phases present very similar features. The similarity of the XANES spectra is associated with analogies in their local structure which can be studied quantitatively using EXAFS data analysis.

![Figure 1](image)

**FIG. 1.** Cu K-edge XANES (left) and derivative (right) spectra of solid $\gamma$-CuBr, $\beta$-CuBr, $\alpha$-CuBr, and liquid CuBr.

**III. EXAFS OF SOLID CuBr: METHODOLOGY**

Low-noise EXAFS spectra of solid CuBr ($c$-CuBr) were analyzed using multiple-scattering calculations (GNXAS) for both Cu K-edge and Br K-edge data.\(^{16,17,14}\) The simultaneous multiple-edge refinement used in our study allowed us to increase the number of useful experimental points and the accuracy in the extraction of the structural parameters.

Structural refinement is based on a fitting procedure that optimizes the agreement between a model absorption signal $\sigma_{\text{mod}}(E)$ and the experimental x-ray-absorption raw data $\sigma_{\text{exp}}(E)$.\(^{16,17}\) The model signal contains the background and structural functions and therefore depends on a specified set of $ρ$ structural parameters $\lambda = (λ_1, λ_2, \ldots, λ_p)$. Both solid and liquid phase model background functions take account of the well-known background features associated with the $[1s3d]$ and $[1s3p]$ double-electron excitations in Br K-edge spectra.\(^{23,24}\) The structural signal is calculated using a multiple-scattering (MS) $n$-body expansion, i.e., defining the individual terms associated with two-atom ($γ(2)$), three-atom ($γ(3)$), and more generally $n$-atom configurations.\(^{16}\) The $n$-body expansion is usually rapidly convergent. Data analysis is carried out by minimizing a $χ^2$-like residual function and standard procedures developed for nonlinear fitting problems are used to obtain the best-fit estimates for the structural parameters and their statistical errors, naturally related to the experimental noise.\(^{17}\) The procedure is easily extended to the case of multiple-edge fitting.\(^{14,15}\) In this case, any $χ^2$-like residual function proportional to

$$R(\lambda) = \sum_{\lambda} \left( \frac{\sigma_{\text{mod}}(E_\lambda) - \sigma_{\text{exp}}(E_\lambda)}{\sigma_{\text{exp}}^2(\lambda)} \right)^2$$

\[(1)\]

can be used to perform a simultaneous structural refinement over a selected number $M$ of independent x-ray-absorption spectra related to the same system. In Eq. (1) the index $i$ runs over the number $N_i$ of experimental energy points $E_i$ of each absorption spectrum $j$. $σ_{\text{exp}}^2(\lambda)$ is the variance associated with the $α_{\text{exp}} - α_{\text{mod}}$ random variable.

In multiatomic systems, as in the present CuBr case, it is possible to derive consistent partial short-range distribution functions with high accuracy. As in the usual single-edge case, use of Eq. (1) allows us to perform a complete statistical analysis of the structural results. The optimal best-fit values $\{λ\} \equiv (λ_1, λ_2, \ldots, λ_p)$ along with their statistical errors including correlation among different parameters can be evaluated as illustrated elsewhere.\(^{17,26}\) Typical errors in the $0.001–0.01$ Å range for first-neighbor bond distances have been found using such $ab\text{ initio}$ multiple-scattering calculations of the x-ray-absorption cross section.

Present calculations of the structural EXAFS signal were performed using the muffin-tin approximation and allowing for a 10% overlap between the muffin-tin spheres. Multiple-scattering two-body $γ(2)$ (Cu-Br, Cu-Cu, and Br-Br) signals related to the first three neighbor shells around the Cu and Br photoabsorbing sites were calculated. The three-body $γ(3)$ involving first-neighbor bonding in the Br-Cu-Br and Cu-Br-Cu tetrahedral configurations were also evaluated.

In our analysis, we took into account of possible anharmonic effects by introducing the adimensional parameter $β$. 

---

Interdipartimentale Grandi Apparecchiature (Università di Camerino).

The Cu K-edge and Br K-edge EXAFS spectra were measured in transmission mode on beamlines D42-EXAFS 1 equipped with a channel-cut Si (331) monochromator and D44-EXAFS 4 equipped with a double-crystal Si (311) monochromator of the Laboratoire pour l’Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France). Low-noise EXAFS spectra were recorded at the temperature of 295, 400, 600, 670, and 793 K. XAS measurements as a function of temperature were performed using a high-temperature setup operating in vacuum and previously used for liquid metals and molten salts.\(^{19-22}\) The measured EXAFS spectra are characterized by a high signal-to-noise (S/N) ratio of $\sim 10^5$ for the Cu K edge and $\sim 10^4$ for the Br K edge.

As is well known, CuBr shows two solid-solid phase transitions characterized by a constant increase of the dc conductivity approaching its superionic $\alpha$ phase. We followed the structural variations in CuBr, recording several XANES (x-ray-absorption near edge structure) spectra.

In Fig. 1 we show some of the XANES spectra (left panel) along with their first derivatives (right panel), recorded as a function of temperature. The $\gamma \rightarrow \beta$ transition ($T = 658$ K) is clearly revealed both in the absorption and in the derivative spectra (see Fig. 1) by the decrease of the height of the main absorption peak around 8984 eV and by the disappearance of the small feature around 8990 eV. The $\beta \rightarrow \alpha$ transition ($T = 742$ K) is also monitored by the almost complete smoothening of the signal above the main absorption peak. The $\alpha$—liquid transition is marked by the softening of the main absorption peak. We notice that near-edge spectra of liquid and high-temperature solid CuBr phases present very similar features. The similarity of the XANES spectra is associated with analogies in their local structure which can be studied quantitatively using EXAFS data analysis.
(skewness) defined as \( \beta = K_3 / \sigma^3 \) where the \( K_3 \) is the third cumulant of the first-neighbor distribution. We modeled the bond length probability density using an Euler \( \Gamma \)-like distribution:

\[
p(r) = \frac{2}{\sigma^3 \beta} \left( \frac{4}{\beta^2} + \frac{(r-R)}{\sigma \beta} \right)^{\alpha/2} - 1 \\
\times \exp \left[ - \left( \frac{4}{\beta^2} + \frac{(r-R)}{\sigma \beta} \right) \right].
\]

The EXAFS signal was averaged over this distribution and multiplied by the coordination number \( N \) \((N=4 \text{ in solid CuBr})\).

A typical refinement of the Br and Cu \( K \)-edge EXAFS spectra near room temperature was performed using nine structural parameters, plus two edge energies \( E_{0,\text{Cu}} \), \( E_{0,\text{Br}} \), and amplitude correction factors \( S_{0,\text{Cu}}^2 \) and \( S_{0,\text{Br}}^2 \). The structural parameters include the first shell and third shell \( R_1 \), \( R_3 \) distances and variances \( \sigma_{1(\text{Cu-Br})}^2 \), \( \sigma_{3(\text{Cu-Br})}^2 \); the skewness parameter of the first-neighbor distribution \( \beta \); the average Cu-Br-Cu and Br-Cu-Br bond angle values \((\theta \approx 109.47^\circ)\) and their angle variances \( \sigma_\theta^2 \). Using this parameterization, the second shell distributions (Cu-Cu and Br-Br) are automatically defined. The total number of the floating parameters is therefore 13 at room temperature, using about 600 experimental energy points. However, due to the relatively large vibrational amplitudes, the structural signal is substantially dominated by the first-shell Cu-Br signal associated with \( R_1 \), \( \sigma_{1(\text{Cu-Br})}^2 \), and \( \beta \) structural parameters. This justifies, \textit{a posteriori}, the use of a diagonal covariance matrix for the thermal average of the three-body signals in the whole temperature range. The fitting procedure that minimizes the difference between the experimental spectrum and the theoretical signal was the last step in our data analysis as illustrated in the next section.

IV. EXAFS OF SOLID CuBr: RESULTS AND DISCUSSION

Simultaneous analysis of Cu \( K \)-edge and Br \( K \)-edge EXAFS data of solid CuBr at room and high temperatures were performed using the methods described in the preceding section. As an example, the result of the multiple-scattering EXAFS data analysis of CuBr at \( T = 295 \text{ K} \) are reported in Fig. 2. The total Cu model signals \( k \chi(k) \), lower curves (fit) in Fig. 2, were calculated using two-body (\( \gamma^{(2)} \)) and three-body (\( \gamma^{(3)} \)) terms associated with the thermodynamic mean.

The two-body \( \gamma^{(2)}_1 \) and \( \gamma^{(2)}_2 \) signals, reported in Fig. 2, for both edges, depend on the first-shell parameters \( R_1 \), \( \sigma_{1(\text{Cu-Br})}^2 \), and \( \beta \). The \( \gamma^{(2)}_2 \) signal (second from the top to the bottom) is associated with the third shell atoms (parameters \( R_3 \), \( \sigma_{3(\text{Cu-Br})}^2 \)). The \( \gamma^{(3)}_1 \) signals are associated with the three-body Cu-Br-Cu (Br-Cu-Br) tetrahedral configurations and contain both the irreducible three-body signal and the two-body Cu-Cu (Br-Br) ones, related to the longest side of the triangle. They depend on the first-shell structural parameters and, additionally, to the angular ones. The last \( \gamma^{(3)}_2 \) signals are the irreducible three-body terms related to the Br-Cu-Br (Cu-Br-Cu) tetrahedral configurations where the photoab-
based on the phonon spectrum at low temperature, reported in Ref. 5. The increase of the bond variance at higher temperature is higher than expected from the harmonic model $s^2 \sim 1.3 \times 10^{-2} \text{Å}^2$, see Ref. 5, confirming the inadequacy of this approach at high temperature.

In Table I we report also the third cumulant $K_3$ of the first-neighbor distribution, directly calculated from the skewness parameter $\beta$ included in the Euler $\Gamma$ function given by Eq. (2). The $K_3$ value obtained here at room temperature coincides within the error with the value reported in Ref. 5 by Tranquada and Ingalls. The third cumulant increases rapidly at higher temperatures, as expected in presence of large anharmonic effects.

EXAFS structural determinations at room temperature reported in Table I are in reasonable agreement with each other. However, present data are obtained by using a sophisticated multiple-edge approach giving us a precise idea of the statistical error and accounting for an asymmetric two-body distribution. For example, the shorter (0.04 Å) first-neighbor distance found in Ref. 6 is perfectly compatible with present determination of the average distance, provided that the asymmetry is taken into account. In fact, the most probable value of the first-shell two-body distribution function $g_{CuBr}(r)$ at room temperature, shown in Fig. 4, is around 2.42 Å. The first-neighbor $g_{CuBr}(r)$ distributions at $T=295$, $T=400$, $T=600$, and $T=670$ K are shown in Fig. 4.

### Table I

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (10$^{-2}$ Å$^2$)</th>
<th>$K_3$ (10$^{-3}$ Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXAFS (this work)</td>
<td>295</td>
<td>2.453(2)</td>
<td>1.00(5)</td>
</tr>
<tr>
<td>400</td>
<td>2.460(4)</td>
<td>1.7(1)</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>600</td>
<td>2.466(7)</td>
<td>2.5(2)</td>
<td>1.3(2)</td>
</tr>
<tr>
<td>670</td>
<td>2.450(7)</td>
<td>2.8(2)</td>
<td>3.5(7)</td>
</tr>
<tr>
<td>EXAFS (Ref. 6) (Cu K edge)</td>
<td>295</td>
<td>2.413</td>
<td>0.73</td>
</tr>
<tr>
<td>(Br K edge)</td>
<td>295</td>
<td>2.422</td>
<td>0.75</td>
</tr>
<tr>
<td>EXAFS (Ref. 5) (Cu K edge)</td>
<td>210</td>
<td></td>
<td>0.23(4)</td>
</tr>
<tr>
<td>295</td>
<td></td>
<td></td>
<td>0.37(5)</td>
</tr>
<tr>
<td>ND (Ref. 1) ($R=\alpha\sqrt{3}/4$)</td>
<td>293</td>
<td>2.4637(1)</td>
<td></td>
</tr>
<tr>
<td>383</td>
<td>2.4667(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>443</td>
<td>2.4713(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>622</td>
<td>2.4859(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ND (Ref. 2) ($R=\alpha\sqrt{3}/4$)</td>
<td>293</td>
<td>2.468(4)</td>
<td></td>
</tr>
<tr>
<td>610</td>
<td>2.481(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>2.494(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>($R=\alpha/2 \sin \psi; \psi=54.735^\circ$)</td>
<td>670</td>
<td>2.498(6)</td>
<td></td>
</tr>
</tbody>
</table>

*FIG. 3.* Comparison between the experimental Cu K-edge EXAFS signals of $\gamma$-CuBr at $T=295$ K (solid line) and $\beta$-CuBr at $T=670$ K (dashed). The change in the phase of the signal is due to the shortening of the most probable value of the first-neighbor Cu-Br distribution.

*FIG. 4.* First-neighbor distribution function $g_{CuBr}(r)$ for solid CuBr as a function of temperature. Notice the shift toward shorter distances of the foot and most probable values of the distribution and the increase of the skewness.
400, 600, 670 K, calculated starting from best-fitting parameters reported in Table I, are shown in Fig. 4. Typical error bars on height of the reconstructed $g_{\text{CuBr}}(r)$ distributions are below 0.5 at the first-neighbor peak distance.

The gradual broadening and the increasing of the asymmetry of the short-range $g_{\text{CuBr}}(r)$ as a function of temperature are clearly visible in Fig. 4. A more pronounced change of the shape is observed in the $\beta$ phase at $T=670$ K. The shift of the foot and of the most probable value of the distribution (about 0.09 Å from room temperature to 670 K) is clearly resolved in present determination. The intensities of the first-neighbor peak are larger than those found by Nield and McGreevy using reverse Monte Carlo (RMC) on ND data. However, as pointed out also by the same authors, the RMC results gave too large values for structural disorder in $c$-CuBr, incompatible with known vibrational properties. The contraction of the first-shell distance at high temperature was already suggested in an older EXAFS study of $c$-CuBr at high temperature, where different structural models were tested. Although no indication of the error bar was given, the best-fit model showed a bond length contraction qualitatively similar to the present one.

As anticipated, the Cu-Br bond length probed by EXAFS is shorter than the corresponding Cu-Br distance calculated using the unit cell parameters obtained by ND measurements. The difference is of about 0.01 Å in the 300–400 K range of temperature and increases at higher temperatures, well outside the statistical uncertainty. In particular, the evident shortening of the bond length in the $\beta$ phase at 670 K (see Table I and Figs. 3 and 4) is not reported in any ND work. These conflicting results can be reconciled taking into account the different nature of the XAS and ND measurements, sensitive to short-range and long-range correlations, respectively. In fact, there is no reason to doubt that ND measurements are able to give correct estimates of the unit cell dimensions. However, precise determination of the short-range distribution can hardly be performed using only those data, especially in such disordered systems. The indication given by EXAFS is that the shape of the first-neighbor distribution function $g_{\text{CuBr}}(r)$ is that given in Fig. 4, but this measurement is very accurate only below 2.6 Å. The existence of a longer tail above 2.6 Å, not accurately determined by EXAFS data and possibly not accounted for by the $\Gamma$ distribution itself, could correct the result on the average distance without affecting the shape of the short-range $g_{\text{CuBr}}(r)$ (even accounting for the coordination number constraint). This interpretation is consistent with the various observations and models proposed about cation disorder in such systems (see, for example, Refs. 1 and 3) and shed some light on the structural mechanisms related to the onset of superionicity. In fact, the mobile ions of the $g_{\text{CuBr}}(r)$ tail coexist with a stronger covalency of the Cu-Br bond. The foot of the $g_{\text{CuBr}}(r)$ distribution shifts to shorter distances, as detected by EXAFS, but the $g_{\text{CuBr}}(r)$ distribution broadens and more atoms are now found at longer distances, in agreement with the ND results.

V. EXAFS OF LIQUID CuBr: METHODOLOGY

Current knowledge about the structure of liquid CuBr ($l$-CuBr) is based on ND data obtained using the isotope substitution technique. Partial distribution functions $g_{\text{CuBr}}(r)$, $g_{\text{CuCu}}(r)$, $g_{\text{BrBr}}(r)$ have been obtained by Allen and Howe measuring the three partial structure factors by isotopic substitution of copper. This investigation revealed that the partial structure factors and distribution functions of CuBr are essentially similar to the CuCl ones. Very recently, an independent estimate of the partial structure factor have been also obtained from anomalous x-ray scattering measurements.

Those compounds are regarded to be as “mainly ionic” also in the liquid state because while the Cu-Cu distribution is featureless, the Cu-Br (Cl) and Br-Br (Cl-Cl) ones are essentially of ionic character. However, in spite of the very good quality of the original diffraction measurements, the derived partial structure factors are affected by a quite large intrinsic statistical noise due mainly to the low contrast provided by the Cu isotopes. Unfortunately, this is an intrinsic limitation of the technique and only in a few selected cases it is possible to prepare suitable samples with high-contrast isotopic substitutions. Anyway, in most cases this is the only way to obtain partial distribution functions.

Short-range properties of disordered systems including liquids are also probed by EXAFS. In ab diatomic liquids, such as CuBr, it is possible to obtain separate structural signals related to $a$-all and $b$-all correlations simply measuring the x-ray-absorption cross section near atomic edges associated with both $a$ and $b$ atoms. High-temperature EXAFS measurements of liquid systems can be easily performed in a large photon energy range (typically above 4 KeV) excluding only the lighter elements.

The EXAFS $\chi(k)$ structural signal is essentially different from the structure factor $S(q)$ measured by diffraction experiments. The photoelectron wave vector $k$ roughly corresponds to $2q$ opening the way to low-noise measurements at higher wave-vector values ($q \sim 20–40$ Å$^{-1}$). The most important difference is about the nature of the kernels relating the atomic distribution functions to the measurements. In fact, limiting ourselves to the two-body distribution function $g_2(r)$ for a homogenous and isotropic system, the EXAFS signal is given by an integral

$$\chi(k) = \int_0^\infty 4\pi r^2 g_2(r) \gamma^{(2)}(r,k)dr,$$  

where the $\gamma^{(2)}(r,k)$ kernel represents the calculated EXAFS oscillating signal related to the presence of a neighboring atom at a given distance $r$ from the photoabsorbing atom, for a given wave vector $k$ of the photoelectron. Generally speaking, definition of $\chi(k)$ contains also terms associated with higher-order distribution functions. However, the $n$-body expansion is rapidly convergent at high $k$ values and for highly disordered systems, in absence of strongly covalent chemical bonds. In these cases, the $\chi(k)$ signal is accurately reproduced including only the two-body distribution. The $\gamma^{(2)}$ signal in Eq. (3) is short-ranged due to the strong interaction between the emitted photoelectron and the other valence electrons. For typical EXAFS photoelectron wave-vector values the mean free path of the photoelectron is in the range 5–10 Å, limiting therefore the structural information content, associated with coherent multiple-scattering effects, to a few
TABLE II. Structural parameters related to the first peak of the partial $g_{\text{CuBr}}(r)$ and $g_{\text{BrBr}}(r)$ distribution functions in l-CuBr as determined by modeling previous data obtained from ND measurements (Ref. 9). Average distance $R$, $\sigma^2$, skewness $\beta$ (dimensionless), and coordination number $N$ are specified for each $\Gamma$ function (peak).

<table>
<thead>
<tr>
<th>Peak</th>
<th>$N$</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (10$^{-2}$ Å$^2$)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{\text{CuBr}}$</td>
<td>I</td>
<td>2.556</td>
<td>2.47</td>
<td>6.67</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>2.055</td>
<td>3.25</td>
<td>12.8</td>
</tr>
<tr>
<td>$g_{\text{BrBr}}$</td>
<td>I</td>
<td>3.25</td>
<td>3.80</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Å from the photoabsorbing sites. On the contrary, the kernel appearing in the relation between $g_2(r)$ and the structure factor $S(q)$

$$S(q) - 1 = \int_0^\infty 4 \pi r^2 [g_2(r) - 1] \frac{\sin(qr)}{qr} dr$$

(4)
is much more sensitive to long-range correlations, especially at low $q$ values. Looking at Eqs. (3) and (4) it is clear that a better structural refinement of highly disordered systems can be carried out using both techniques. They are really complementary in the sense that EXAFS is particularly sensitive to short-range order, i.e., to the characteristics of the chemical bond, but it is almost blind to longer range correlations, where neutron or x-ray diffraction measurement can provide reliable structural refinement.

In this work we present a refinement of the partial pair distribution function obtained by neutron diffraction. Of course, EXAFS refinement will be limited to the short-range shape of the distributions. The original positive-defined maximum entropy Cu-Br, Br-Br, and Cu-Cu partial distribution functions derived by Allen and Howe are reported in Fig. 5. A suitable method to perform a realistic refinement consists in the decomposition of the distribution functions into short-range peaks and long-distance tails. This method has been successfully applied to study short-range correlations in several elemental and binary liquids.

The experimental EXAFS signal is practically insensitive to the long-range tails, that are used only to guarantee the correct limit at long distances of the refined distribution functions. A convenient decomposition of the partial distribution functions is shown in Fig. 5, where the solid curves are short-range peaks ($g_{\text{CuBr}}^{(S)}$, $g_{\text{BrBr}}^{(S)}$, modeled as Euler $\Gamma$-like distributions (see Sec. III), and the dot-dashed curves are the long-range oscillatory tails. We used two $\Gamma$ functions to model with higher accuracy the first-neighbor $g_{\text{CuBr}}^{(S)}$ Cu-Br peak, to which the EXAFS signal is more sensitive. Instead, we used a single $\Gamma$ function to model the rise of the first $g_{\text{BrBr}}^{(S)}$ peak. No first-neighbor peak is separated for the Cu-Cu component. Best-fit $N$, $R$, $\sigma^2$, and $\beta$ structural parameters defining the $\Gamma$ functions [see Eq. (2)] describing the short-range pair distributions in l-CuBr are reported in Table II.

This decomposition was used to calculate the EXAFS signal related to the $a$ (Cu or Br) component according to the following expression:

$$\chi_a(k) = \int_0^\infty dr 4 \pi r^2 \rho_g g_{ab}^{(S)}(r) \gamma_{ab}^{(2)}(r,k)$$

$$+ \int_0^\infty dr 4 \pi r^2 \rho_p g_{ab}^{(S)}(r) \gamma_{ab}^{(2)}(r,k)$$

$$+ \langle \gamma_{ab(\text{tail})}^{(2)}(k) \rangle + \langle \gamma_{aa(\text{tail})}^{(2)}(k) \rangle + \cdots ,$$

(5)

where $\rho_g$ and $\rho_p$ are the partial atomic densities and $\gamma_{ab}^{(2)}$ are the effective two-body MS signals resulting from the integrals involving the tails of the partial distribution functions. The $\gamma_{ab}^{(2)}$ signals obtained using the decomposition of the partial distribution functions of Fig. 5, appearing in the right-hand side of Eq. (5), are the upper curves of Fig. 6. Of course, the dominant contributions are those associated with the first-neighbor distributions. Here and in the following the $g_{\text{CuBr}}^{(S)}$ is considered as a single term, although it was modeled as a sum of $\Gamma$ functions, because the contribution associated with the smaller peak in the $g_{\text{CuBr}}^{(S)}$ of Fig. 5 is practically negligible.

The experimental (expt) and calculated (ND) EXAFS $k\chi(k)$ Cu and Br K-edge structural signals in l-CuBr at 793 K are compared in Fig. 6 (bottom). The agreement is very poor. The amplitude of the calculated signal is roughly the same as found in other purely ionic systems such as KBr (Ref. 22) or RbBr (Refs. 18, 15) but that of the experimental spectrum is at least five times bigger. A refinement of the short-range structure is clearly necessary to explain the EXAFS data.

VI. LIQUID CuBr: RESULTS AND DISCUSSION

Using the decomposition reported in Eq. (5) of the preceding section, it is possible to refine the short-range part $g_{\text{CuBr}}^{(S)}(r)$ of the radial distribution. Physical constraints on the $g(r)$ shape, related to the correct thermodynamic limit ($q \to 0$ in the structure factor) can be used allowing a reduction on the number of floating parameters associated with the short-range peaks and consistency with known thermodynamic properties such as density and compressibility.

In particular, constraints on the structural parameters illustrated in Ref. 25 are valid also for the two-component charged liquid under consideration, because the $q \to 0$ limit of the partial structure factors is still $pk_BT K_T$ where $K_T$ is the isothermal compressibility.  In the case of the short-range $g_{\text{CuBr}}^{(S)}(r)$, described by two $\Gamma_1$ and $\Gamma_2$ functions (see Fig. 5), the constraints are $\Delta(N_1 + N_2) = 0$ and $\Delta[N_1(R_1^2 + \sigma_1^2) + N_2(R_2^2 + \sigma_2^2)] = 0$. The coordination number of the short-range $g_{\text{CuBr}}^{(S)}(r)$, described by a single $\Gamma$ function, is also kept fixed. The total number of floating parameters associated with both short-range distribution functions is 9.

In Fig. 7 the best-fit results for l-CuBr are reported. As in Fig. 6, the calculated $\gamma_{ab}^{(2)}$ signals are associated with the short-range peaks of Fig. 5. The refinement process shows that both Cu and Br K-edge spectra of l-CuBr can be explained only enhancing the first-neighbor Cu-Br contribution $\gamma_{ab}^{(2)}$. As a matter of fact, these $\gamma_{ab}^{(2)}$ signals (upper curves in Fig. 7) dominate the two EXAFS spectra in the whole wave-
vector range. The Br-Br peak and the tail components are practically negligible. There is no evidence of a Cu-Cu signal while a quite small signal related to the $g_{\text{BrBr}}(r)$ is found to contribute to the Br $K$-edge EXAFS. Calculated and experimental $k\chi(k)$ spectra are in excellent agreement, as shown by the difference spectrum $k[\chi_{\text{expt}}(k)−\chi_{\text{fit}}(k)]$ (residual, bottom curve) which contains only statistical noise.

Best-fit structural parameters defining the short-range $g^{(s)}$ peaks are reported in Table III. As mentioned above, the fitting was performed keeping the coordination numbers $[N_1+N_\Pi$ for $g_{\text{CuBr}}(r)$ and $N$ for $g_{\text{BrBr}}(r)]$ fixed to the original values (see Table II). Moreover, fulfillment of the second physical constraint $\Delta[N_1(R_1^2+\sigma_1^2)+N_\Pi(R_\Pi^2+\sigma_\Pi^2)]=0$ reduces again the number of parameters defining the first $g_{\text{CuBr}}$ peak. In our case, we imposed the second $R_\Pi$ distance to be implicitly defined by the values of the other parameters. Looking at Table III we find evident differences with the original values derived by ND data. Differences are especially important for what concerns the first $g\chi$ function describing the first-neighbor $g_{\text{CuBr}}$ peak. In fact, the variance $\sigma^2$ is reduced to about 1/3 of the original value, the partial $(N_1)$ coordination number increases by about 20%, the skewness parameter $\beta$ increase considerably, and the average bond length is slightly shifted toward shorter values. On the other hand, EXAFS results are found to be compatible within the errors with the original $g_{\text{CuBr}}(r)$ (see also Table II) and $g_{\text{BrBr}}(r)$ (not refined in the present study) distributions shown in Fig. 5. Hence, we discuss in detail only the results about the $g_{\text{CuBr}}(r)$ distribution, for which changes outside the statistical uncertainty were found from EXAFS refinement.

The reconstructed $g_{\text{CuBr}}(r)$ of l-CuBr is shown in Fig. 8, lower panel, and it is compared with that determined using ND (crosses) and with the first-neighbor peak of solid CuBr at $T=670$ K (dots). The EXAFS $g_{\text{CuBr}}(r)$ shows a narrower well-defined first-neighbor peak of about 0.3 Å of full width at half maximum ($\sigma\sim0.16$ Å). Error bars in Fig. 8 take into account the statistical uncertainty on the structural parameters of Table III. However, the remarkable difference be-
obtain EXAFS signals differing of nearly one order of magnitude (see Figs. 6 and 7) for short-range distributions giving very similar $S(q)$ structure factors. Present EXAFS results show unambiguously that the tendency to form nearly covalent bonds, already present in high-temperature solid CuBr, is maintained in liquid CuBr as well. The transition from solid to liquid CuBr appears to be a quasicontinuous process for what concern short-range ordering, leading to shorter bond lengths but also to broader tails. Increase of the conductivity in the high-temperature solid and liquid phases can be then associated with these long-range tails which contains a large fraction of practically uncorrelated ions (about 1/4 for a typical fourfold first-neighbor coordination in the liquid phase).

VII. CONCLUSION

A detailed study of the short-range structure of the CuBr superionic compound in its solid and liquid phases has been presented. Low-noise Cu and Br $K$-edge XAS data of CuBr in the 300–793 K temperature range have been collected and analyzed using an advanced multiple-edge method using multiple-scattering theory (GNXAS).

XAS data have been found to be extremely sensitive to the details of the first-neighbor two-body distribution $g_{\text{CuBr}}(r)$, which has been modeled as an Euler $\Gamma$-like asym-

FIG. 7. Cu and Br $K$-edge EXAFS $k\chi(k)$ experimental data (expt) of liquid CuBr at $T=793$ K compared with the best-fit multiple-scattering $k\chi(k)$ signal (fit). Major changes are found in the CuBr $\gamma^{(2)}_g$ contribution (uppermost curves) associated with the first-neighbor peak (see Fig. 6 and text). The agreement between calculated and experimental spectra is remarkably good, as shown by the lowermost curves (residual).

between the EXAFS and ND determinations is not particularly surprising. In fact, the sharper EXAFS $g_{\text{CuBr}}(r)$ is perfectly compatible with the original ND data, within the noise level. In Fig. 8, upper panel, we compare the experimental $S_{\text{CuBr}}(q)$ ND data with the curve obtained through back transformation from the $g_{\text{CuBr}}(r)$ reconstructed by EXAFS (lower panel) and with the original $S(q)$ derived in Ref. 9 using the maximum-entropy method. EXAFS and maximum entropy curves are both compatible with experimental data within the noise level, as confirmed by $\chi^2$ analysis. These two curves, however, correspond to remarkably different short-range $g_{\text{CuBr}}(r)$ curves as shown in Fig. 8, lower panel.

The unique EXAFS sensitivity to short-range order, due to the nature of the kernel in Eq. (3), makes it possible to

TABLE III. Structural parameters defining the first peak of the partial $g_{\text{CuBr}}(r)$ and $g_{\text{BrBr}}(r)$ distribution functions in I-CuBr as determined by EXAFS data analysis. Average distance $R$, variance $\sigma^2$, skewness $\beta$ (dimensionless), and coordination number $N$ are specified for each $\Gamma$ function (peak). Statistical errors on derived parameters are shown in brackets. Only nine independent parameters are actually independent (see text).

<table>
<thead>
<tr>
<th>Peak</th>
<th>$N$</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{\text{CuBr}}$</td>
<td>I</td>
<td>3.0(2)</td>
<td>2.435(5)</td>
<td>2.6(1)</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.6(2)</td>
<td>3.45(15)</td>
<td>12(3)</td>
</tr>
<tr>
<td>$g_{\text{BrBr}}$</td>
<td>I</td>
<td>8.79</td>
<td>4.1(2)</td>
<td>90(50)</td>
</tr>
</tbody>
</table>
metric function in the solid phases. High-temperature spectra show a clear shortening of the Cu-Br bond length as detected by EXAFS. This effect is clearly observed in the raw data and is assigned to an increased asymmetry of the first-neighbor distribution at high temperature. In particular, the foot of the reconstructed $g_{CuBr}(r)$ distribution of solid CuBr is shifted of about 0.09 Å toward shorter distances from room temperature to 670 K, whereas the long-range part of distribution broadens with temperature. This is due mainly to the combined effect of increasing width and asymmetry of the first-neighbor distribution (distance variance $\sigma \sim 0.028$ Å$^2$ and third cumulant $K_3 \sim 0.0035$ Å$^3$ at $T = 670$ K). Variance and skewness of the first-neighbor distribution have been accurately measured at various temperature in the $\gamma$ and $\beta$ phases.

Substantial agreement with previous diffraction studies has been found. The shortening of the effective Cu-Br bond length probed by EXAFS is associated with the large asymmetry of the distribution at high temperature. However, the average distance is still compatible with ND data due to broadening of the long-range tail. This result shows the large complementarity between XAS and diffraction structural techniques and shed new light on the structural mechanism beyond superionicity. The increasing asymmetry of the Cu-Br distribution, leading to an increase of the weight of uncorrelated mobile ions, is also associated with the shift toward shorter distances of the first-neighbor peak.

Multiple-edge EXAFS data of liquid CuBr have been analyzed using partial distribution functions derived from ND measurements as a starting point. The short-range partial $g_{CuBr}(r)$ distribution has been accurately measured by EXAFS and compared with previous results. $g_{BrBr}(r)$ and $g_{CuCa}(r)$ have been found to be consistent with previous data. We show that the first-neighbor peak is much narrower than previously reported ($\sigma \sim 0.016$ Å), and slightly shifted to shorter values. However, the original structure factor measured by ND is still compatible with present XAS data. The intrinsic error in the short-range structure determination by ND is therefore quite large, due to the low contrast in the isotopes scattering lengths, which is unfortunately a rather general occurrence. This is a typical case in which very precise structural information can be gained by XAS experiments taking advantage of its unique short-range sensitivity. These results are relevant to the understanding of the nature of the like-unlike ion interaction in ”superionic” melts such as l-CuBr or liquid CuCl. In fact, simple ionic interatomic potentials can not account for the observed shape of the first peak of the $g_{CuBr}(r)$, which instead indicates surviving of nearly covalent bonds in the liquid phase. Theoretical models including nonionic interactions should be devised to explain the experimental $g_{CuBr}(r)$. New theoretical and experimental investigations on solid and liquid superionic systems are stimulated by present results.

**ACKNOWLEDGMENTS**

We would like to thank the LURE staff of the beamlines D44-EXAFS 4 and D42-EXAFS 1 and in particular A. Traverse and F. Villain. We wish also to thank Roberto Tossici (Università di Camerino) for his help in the initial stage of the research.