The crystal structure of polycrystalline powder \( \kappa-(\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2\text{Br} \) studied by high energy x-ray diffraction

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Abstract. We present a structural investigation of the organic charge-transfer salt superconductor \( \kappa-(\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2\text{Br} \) at a temperature of 90 K using high energy (90 keV) powder x-ray diffraction. With this approach we access the scattering profile over a wide range in \( Q \)-space (from \( \sim 0.3 \) to 19 Å\(^{-1} \)). Overall, the observed scattering intensity is understood as a superposition of Bragg diffraction from a crystalline phase superimposed onto a large quasi-amorphous signal, indicative of short range order effects in our powder material. We discuss implications of these findings regarding the structural properties of this material.

In recent years, the organic charge-transfer salts \( \kappa-(\text{BEDT-TTF})_2X \) with \( X = \text{Cu(NCS)}_2 \), \( \text{Cu[N(CN)]}_2\text{Br} \) and \( \text{Cu[N(CN)]}_2\text{Cl} \) stood in the focus of intensive research efforts \([1, 2, 3, 4, 5]\). In these studies, the prime topics of interest were their exotic superconducting and normal state properties, resembling to some degree the high-\( T_c \) cuprates. The materials \( X = \text{Cu[N(CN)]}_2\text{Br} \), \( \text{Cu[N(CN)]}_2\text{Cl} \) crystallize in an orthorhombic crystal structure, space group \( Pnma \) (\( Z = 4 \)) \([6]\). The structure contains alternating layers of a conducting network of cations \( (\text{S}_8\text{C}_{10}\text{H}_8)_2^+ \) (bisethylenedithiotetraethylfulvalene, abbreviated BEDT-TTF) and insulating polymeric anion chains \( X^- \). This layered crystal structure causes these materials to behave in a quasi-twodimensional fashion in terms of their electronic properties. Compositional modifications by replacing the anion \( X = \text{Cu[N(CN)]}_2\text{Cl} \) with \( \text{Cu[N(CN)]}_2\text{Br} \) or \( \text{Cu(NCS)}_2 \) tunes the ground state from an antiferromagnetic insulator into correlated metal states. Such behavior is assumed to reflect a bandwidth-controlled Mott transition \([7]\).

The conceptual phase diagram presented in Ref. \([7]\) simplifies the experimental situation, with spatial inhomogeneities and percolating states appearing close to the Mott transition in experimental studies (see for instance Refs. \([8, 9]\)). The observation of inhomogeneous states opens up the question of the interplay of structural and electronic inhomogeneities, this in particular in view of the observation of glass-like transitions in the series of compounds \([3, 10]\). So far, in detailed structural investigations using x-ray laboratory techniques for instance on \( \kappa-(\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2\text{Br} \) (abbreviated \( \kappa-\text{Br} \) hereafter) the glass-like transition at \( T_g \sim 77 \) K could be identified in physical properties such as the temperature dependence of the lattice
parameters (which at 100 K are $a = 12.884(5)$ Å, $b = 29.581(8)$ Å, and $c = 8.484(4)$ Å [10]). Yet, these studies did not unambiguously reveal the microscopic nature of the glass-like transition. Only, the notion of a configurational freezing-out of the terminal ethylene groups of the BEDT-TTF molecule at $T_g$, as it was proposed previously [3, 11, 12, 13], appears to be inconsistent with the experimental data.

In this situation we decided to extend our structural investigation of the glass-like transition in $\kappa$-Br by using synchrotron-based x-ray techniques. This approach enables us to use high energy (90 keV) x-ray diffraction, which in turn allows to study the scattering profile of $\kappa$-Br over a wide parameter range of the scattering vector $Q$ with high statistics. Here, we present first results of our study.

For the experiment we have used the beamline ID15B at the European Synchrotron Radiation Facility, which offers as operation modes monochromatic x-ray radiation at energies of 30, 60 or 90 keV (a description of the beamline set-up can be found in Ref. [14]). In our case, we have carried out a standard powder diffraction experiment at highest available energy, using an on-line image plate detector to record the Debye-Scherrer rings.

The powder sample $\kappa$-Br has been obtained from single crystals grown in Frankfurt as described in Ref. [4]. These crystals were crushed to powder by hand within a few minutes using a mortar and pestle. The powder was filled into a thin glass capillary, which was installed on the sample holder of a closed cycle cryostat and could be spun within the horizontal plane. The sample holder of the cryostat (lowest achievable temperature $\sim 20$ K) was covered by a can with x-ray transparent windows. Size homogeneity and random arrangement of the powder was verified by checking the Debye-Scherrer diffraction patterns for an inhomogeneous intensity distribution. Since in a first experiment some intensity inhomogeneity was observed, the sample $\kappa$-Br was crushed another time for a few minutes by hand with mortar and pestle. Subsequently, the Debye-Scherrer ring intensity was evenly distributed.

For the experiment temperatures in the range 20 to 120 K were set and the Debye-Scherrer diffraction patterns for $\kappa$-Br were recorded by the image plate detector under continuous spinning of the capillary. By performing a numerical integration of the intensity measured at the detector along the trace of the diffraction cone with scattering vector $Q$ we arrive at the common representation of the intensity distribution $I(Q)$ of a Debye-Scherrer experiment. As an example we present the data for $\kappa$-Br measured at 90 K in Fig. 1 (green line).

Subsequently, a diffraction pattern was taken for the same experimental geometry with only an empty glass capillary installed in the sample holder. Again, in the same way as for the filled capillary a numerical integration of the measured intensity was performed, with the resulting data included in Fig. 1 (red line). In a next step, the data for the empty capillary is subtracted from that of the filled one, in order to correct for scattering contributions from the experimental set-up. We include the corrected data in Fig. 1 (black line).

Clearly, and especially for $Q \leq 4$ Å$^{-1}$, in Fig. 1 a large number of Bragg peaks can be identified. The positions of all these peaks can be accounted for with the orthorhombic crystal structure of $\kappa$-Br using lattice parameters of $a = 12.91$ Å, $b = 29.82$ Å, and $c = 8.524$ Å, which is in good agreement with the values reported in Ref. [10]. However, from Fig. 1 it is also apparent that even our data of $\kappa$-Br corrected for scattering from the set-up exhibits an additional and large quasi-amorphous scattering contribution. Without further information, the precise $Q$ dependence of this contribution is not known. However, from Fig. 1 it can be estimated that for $Q \leq 4$ Å$^{-1}$ the quasi-amorphous intensity in absolute counts is of the same order of magnitude as the intensity of well-defined Bragg peaks, while for larger $Q$ values amorphous contributions dominate the scattering profile. As consequence, these large amorphous contributions prohibit to carry out a full structural refinement of our data. We can, however, model our data by separating out different contributions.

In Ref. [10] we have obtained detailed structural information on $\kappa$-Br. We use these positional
parameters from Ref. [10] together with the experimental lattice parameters to calculate the intensity distribution for perfectly crystalline material in a powder diffraction experiment. Next, we *ad-hoc* choose a $Q$-dependent profile, which - by adding it to the calculated powder diffraction profile of $\kappa$-Br - produces a reasonable description of our data. Our procedure is illustrated in Fig. 2, where we plot our data (+) together with the quasi-amorphous scattering profile (blue line) and the resulting fit of the data (black) for $Q \leq 4.2$ Å$^{-1}$ (a.) and the full spectrum (b.).

From Fig. 2(a) it is apparent that for small $Q$ values we can reproduce peak positions and almost quantitatively peak intensities for our powder sample $\kappa$-Br, if we assume a scattering profile with a broad quasi-amorphous shape (maximum of about 10000 counts in the range $Q \sim 2$ Å$^{-1}$), together with some broad peaks (up to 20000 counts close to 2 Å$^{-1}$). On top of this quasi-amorphous part sits our scattering intensity from a crystalline phase with maximum peak intensities up to 20000 counts. Moreover, the experimental data for larger $Q$ values must almost entirely be attributed to a quasi-amorphous phase (see Fig. 2(b)). In other words, our data parameterization suggests that our powder sample $\kappa$-Br, produced from single crystalline material by crushing for a few minutes by hand using mortar and pestle, contains a significant amount of quasi-amorphous or strongly distorted crystalline phase.

It is well known that crushing eventually will cause a destruction of the crystalline lattice, and thus produce amorphous material (see Refs. [15, 16]). However, as indicated in Refs. [15, 16], in these cases crushing is performed by milling the material over a long period of time (a few to a thousand hours), rather than doing it by hand for a few minutes. This implies that the organic superconductors studied here exhibit an extraordinary structural sensitivity to metallurgical treatment such as crushing. This observation of course is in line with the general experience researchers have while working with these systems, with for instance reports of dependencies of physical properties on thermal treatments etc. [3, 4, 11, 12]. It suggests that in these cases the

![Graph](image_url)
difference in sample treatment corresponds to a difference in the density of dislocations, lattice faults etc., which apparently are easy to be produce in these organic salts.

Regarding our present study, the next step will be to analyze the temperature dependence of our structural data. In particular, it will be worthwhile to determine if there are features to be observed for the Bragg peak intensities or amorphous scattering contributions of $\kappa$-Br, which reflect the glass-like transitions observed for single crystalline material.

This research was supported by the DFG under Grant No. SU229/8-2. We acknowledge fruitful discussions with R. Feyerherm.

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