Crystal structure and distortion of superconducting Cu$_x$Bi$_2$Se$_3$

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The crystal structure of the candidate topological superconductor Cu$_x$Bi$_2$Se$_3$ was studied by single-crystal neutron diffraction using samples obtained by inserting the Cu dopant electrochemically. Neither structural refinements nor calculated scattering-density maps find a significant occupation of Cu at the intercalation site between the quintuple layers of Bi$_2$Se$_3$. Following Bragg reflection intensities as function of temperature, there is no signature of a structural phase transition between 295 and 2 K. However, the analysis of large sets of Bragg reflections indicates a small structural distortion breaking the rotational axis due to small displacements of the Bi ions.

I. INTRODUCTION

The discovery of superconductivity in Cu-intercalated Bi$_2$Se$_3$ attracts strong interest, because these materials are proposed to be candidates for topological superconductivity. Topological superconductivity is caused by a non-trivial topology in the superconducting wavefunction and is expected to lead to novel phenomena and quasiparticles, of which Majorana fermions are most prominent. Fu and Berg analyzed the pairing symmetry in Cu$_x$Bi$_2$Se$_3$ and conclude that the strong spin-orbit coupling in doped Bi$_2$Se$_3$ can result in odd-parity superconductivity with such non-trivial topology. The spin-orbit coupling circumvents a strict separation in singlet and triplet pairing, and the spin-orbit-coupled internal degree of freedom takes a triplet. Besides through Cu intercalation, Bi$_2$Se$_3$ exhibits superconductivity also for S or Ni insertion. Support for unconventional superconductivity with spin-triplet like pairing is detected in temperature dependent NMR Knight shift experiments, which find only a small change below $T_c$ in the electronic spin susceptibility for most directions of the magnetic field parallel to the layer. This experiment also observes a two-fold axis of the Knight shift in the superconducting state, which indicates that the rotational three-fold symmetry is broken below $T_c$. The superconducting transition can thus be associated with nematicity. In the meantime, there is strong support that the superconducting state in all three doped Bi$_2$Se$_3$ systems exhibits a lower symmetry. In this nematic superconductivity the threefold rotation axis of the parent material is broken most likely by the anisotropy of the gap amplitude (not only the phase). Critical magnetic fields exhibit a huge in-plane anisotropy following only a two-fold axis. Also, the magnetization, resistivity and magnetoresistance exhibit two-fold symmetry leading to the conclusion that the nematicity is essential for the superconducting phase in doped Bi$_2$Se$_3$.

An improvement of the sample preparation by electrochemical intercalation and by an annealing step considerably raised the shielding fraction in Cu$_x$Bi$_2$Se$_3$. These improved samples exhibit a well-defined anomaly in the specific heat that documents the bulk nature of the superconductivity. Superconductivity occurs in a broad doping range of $0.1 \leq x \leq 0.5$ and the transition temperature varies less sharply with doping than the shielding fraction. Furthermore, the charge carrier density does not follow the amount of doping but stays nearly constant at a rather low value of about $10^{20}$ cm$^{-3}$. So far, the three different insertions to induce superconductivity in Bi$_2$Se$_3$ seem to result in essentially the same physical properties, but the Sr and Nb samples are less air-sensitive and superconducting crystals can be grown.
The parent compound Bi$_2$Se$_3$ crystallizes in the rhombohedral space group $R\bar{3}m$ and the structure consists of quintuple layers of Bi$_2$Se$_3$ that are bonded perpendicular to the layers only through the weak van-der-Waals interaction, see Fig. 1(b) [12]. In spite of the enormous impact of these candidate topological superconductors, there is little knowledge about the crystal structure in the doped materials. Hor et al. deduced from an increase in the $c$ lattice parameter that Cu would occupy an intercalation position in the van-der-Waals gap between two quintuple layers, at position (0,0,1/2) see Fig. 1(b) [12], but scanning tunnel microscopy, angle resolved photoemission spectroscopy and $ab$ initio density functional theory proposed other positions - intercalating and interstitial ones - for the dopant [13]. Li et al. report a structural analysis of Sr$_2$Bi$_2$Se$_3$ by high-resolution transmission electron microscopy and DFT calculations concluding that the Sr dopant is not occupying the intercalation position [13]. In addition, a small structural distortion in the Sr$_2$Bi$_2$Se$_3$ lattice of about 0.02% was deduced from a high resolution X-ray study of $d$-values at ambient temperature [13].

Here we report on neutron diffraction studies on superconducting Cu$_x$Bi$_2$Se$_3$ crystals at room temperature, as well as at temperatures slightly above and below the superconducting transition. Cu-doped Bi$_2$Se$_3$ is the prototype compound of this family of unconventional superconductors and such samples are used in various experiments including those documenting the nematic character for the first time. Therefore, we consider it most important to also clarify the crystal structure and the position of the dopant for this material. We cannot detect Cu occupation at any of the proposed intercalation and interstitial sites, and there is no indication for a structural phase transition between room temperature and 2 K. However, structural refinements with large data sets improve when the symmetry is lowered to monoclinic.

II. EXPERIMENTAL

Bi$_2$Se$_3$ single crystals were grown from a stoichiometric melt. Pieces of the single crystals were electrochemically doped by Cu using a saturated solution of CuI in CH$_3$CN. Typical stoichiometries for superconducting Cu$_x$Bi$_2$Se$_3$ lie in the range 0.12 $\leq x \leq$ 0.6, and shielding fractions of up to 50% can be achieved by this technique but the large crystals required for the neutron diffraction experiment yield lower values. Details of the growth process can be found in reference [10].

The large samples used for neutron diffraction experiments are shown in Fig. 2. The Cu doped samples are sensitive to air; therefore, for storage and transport they need to be sealed in glass tubes. They were cleaved and cut to exhibit a plate-like shape before the intercalation step and the direction of smallest extension is the $c$ direction of the hexagonal cell. Sample S1 exhibits a Cu amount of $x = 0.30(1)$ ($T_c=3.1$ K), for sample S2 it amounts to $x = 0.33(1)$ ($T_c=3.6$ K) and for sample S3 to $x = 0.31(1)$ ($T_c=3.4$ K). Throughout the paper numbers in parenthesis give the error bars of the last digits. Superconducting transition temperatures and shielding fractions were measured in a SQUID magnetometer and the results are shown in Fig. 3. The Cu concentration can be determined by weighting the crystals during the intercalation step but thus only corresponds to the average over the entire crystal.

Single crystal neutron diffraction was carried out with the three Cu$_x$Bi$_2$Se$_3$ crystals on the single-crystal neutron diffractometer D2(b) at the Institut Laue Langevin using a wavelength of 0.84 Å. The sample S1 was measured at a temperature of 300 K, with a pinhole of 5 mm diameter and at the temperatures of 1.9 K and 4.4 K with a pinhole of 6 mm. During the data collection at 300 K, a slight misalignment of the pinhole was detected that however turned out insignificant for the data quality. At 1.9 K and 4.4 K, most of the reflections were collected with exposure times between 3 s and 6 s per point in a combined $\omega$-2$\theta$ scan with $n$ between 0 and 20, at 300 K exposure times amounted to between 5 s and 8 s. With sample S2 only temperature dependent measurements of Bragg intensities were performed. Also with the other two samples Bragg intensities were measured as function of temperature in order to search for a structural phase transition. For sample S3, the optimum pinhole of 7 mm diameter was determined by Remminger scans. At 300 K, most of the reflections were collected with exposure times between 3 s and 5 s per data point, and at 2 K with times between 2 s and 7 s.

![Fig. 2. Cu$_x$Bi$_2$Se$_3$ samples for neutron diffraction. (a) S1, (b) S2, (c) S3. Since the samples are air sensitive, the photos of the last two samples were taken with the samples sealed in glass tubes and mechanically protected by quartz wool.](image)
FIG. 3. Zero-field cooled (ZFC) magnetization curves measured with the three single crystals used in the neutron diffraction experiments. The magnetic field of 0.2 mT was applied along the planes. Shielding fractions (SF) are given in the legend for T = 1.78 K.

The intensity data were absorption corrected using the program DATAP. For sample S1, the orientation was exactly known, and a box geometry with a length of 2.82 mm, a width of 1.55 mm and a thickness of 0.73 mm was applied. The length and width was determined optically, and the thickness was calculated via the mass of 25.23 mg assuming a density of 7.90 g/cm$^3$ (where the Cu doping with $x = 0.30$ is taken into account). Sample S3 exhibits a more irregular plate-like shape and the area was determined optically to amount to 8.54 mm$^2$. Via the mass of 46.22 mg and the density, the thickness of 0.69 mm was determined.

III. RESULTS AND DISCUSSION

1. Vacancies and possible Cu positions

First refinements of the crystal structure were performed in space group $R\bar{3}m$ that is reported for the parent compound and that allows for various possible Cu positions. Rhombohedral crystals in general can exhibit two twins corresponding to obverse and reverse setting. The refinements of these twinning fractions for sample S1 yield $-0.99(1.23)$ % at 1.9 K, $-0.02(1.65)$ % at 4.4 K and $0.46(23)$ % at 300 K for the reverse setting. The corresponding refinements for sample S3 yield fractions $0.39(1.30)$ % at 2 K and $-0.82(1.99)$ % at 300 K for the reverse setting. Thus, the samples do not exhibit obverse/reverse twinning.

Se vacancies are supposed to play an important role for transport properties in pure Bi$_2$Se$_3$. Therefore, the occupation of the two Se sites were refined. For sample S1 at a temperature of 1.9 K, 4.4 K and 300 K, the occupation of the Se2 site is 1.011(12), 0.995(16) and 1.002(16), respectively, and the occupation of the Se3 site is 0.999(11), 0.998(14) and 0.985(16), respectively. For sample S3 at 2 K and 300 K, the occupation of the Se2 site is 1.008(10) and 1.003(15), respectively, and the occupation of the Se3 site is 0.989(10) and 1.001(14), respectively. These values are consistent with full occupation. Thus, no Se vacancies could be detected by neutron diffraction.

These refinements not only exclude Se vacancies but also a significant amount of Bi vacancies. We estimate a possible substitution of Bi through Cu by their diffractive constant and without considering the other Cu positions (i) to (v) that are all located at a Wyckoff position 6d, which is reported for the par-}

TABLE II. Occupancies (given in percent of full occupation) of the possible Cu positions (i) to (v) that are all located at a Wyckoff position 6d from refinements in space group $R\bar{3}m$. There is no significant deviation from zero. Each value was determined by a separate refinement without considering the other Cu positions.

|       | Cu(i) | Cu(ii) | Cu(iii) | Cu(iv) | Cu(v) |
|-------|-------|--------|---------|--------|-------|
| S1 4.4 K | 0.4(4) | 0.1(4) | 0.6(4)  | 0.4(4) | -0.37(33) |
| 300 K   | 0.4(5) | 0.3(5) | 0.2(5)  | -0.2(5) | -0.1(4)  |
| S3 300 K | 0.6(5) | 0.5(5) | 0.8(5)  | 0.6(5) | -0.2(4)  |

Cu intercalation in the van-der-Waals gap is expected to enhance the thickness of the van-der-Waals gap and thus to cause an increase of the lattice parameter. For pristine Bi$_2$Se$_3$, the lattice constants $c = 28.636(20)$ Å$^2$, 28.615(2) Å$^2$ and 28.666(1) Å$^2$ were reported and for Cu$_{0.5}$Bi$_2$Se$_3$, the parameter increases to 28.736(1) Å.$^2$. Le Bail refinements of (00l) scans performed on a D5000 X-ray diffractometer with our single crystals yield a lattice constant $c = 28.5990(8)$ Å for undoped Bi$_2$Se$_3$ and 28.683(2) Å for Cu$_{0.3}$Bi$_2$Se$_3$ confirming the increased lattice constant $c$ due to the insertion of Cu. $\Delta c = 0.084 Å \sim 2.9 \cdot 10^{-3}c$.

The occupation of the most obvious intercalation position at 3b (0,0,1/2) was examined with the five data sets obtained on two distinct samples by comparing refinements with full occupation, with partial occupation and without any Cu at this position. For the Cu atom, the displacement parameter was fixed to isotropic $U = 0.005 Å^2$ for the high temperature 300 K respectively $U = 0.0025 Å^2$ for the low temperatures 1.9 K, 2 K and 4.4 K. The results are shown in Table V in the Appendix. The five data sets consistently exclude a significant presence of Cu at this position. By combining scanning tunnel microscopy, angle resolved photoemission spectroscopy and ab initio density functional theory,
Wang et al. conclude that the most probable sites for the Cu atoms are two interstitial sites within the quintuple layers and three intercalated sites between the quintuple layers. From the caption of Fig. 4 in reference 14, it is possible to reconstruct these coordinates. Using the structural parameters from reference 17, one gets the following positions: The interstitial atom Cu(i) is located at the position 6c (1/3, 2/3, 0.36127(34)), and the other interstitial position Cu( ii) is 6c (0, 0, 0.34032(33)). The coordinates of the three intercalated atoms are: 6c (0, 0, 0.1321(15)) for Cu(iii), 6c (2/3, 1/3, 0.2047(15)) for Cu(iv) and 6c (1/3, 2/3, 0.1733(15)) for Cu(v). Other possibilities can be found in references 24 and 18. All positions proposed in reference 14 are tested via structural refinements. A significant occupation was detected in none of these positions, see table I.

Symmetrized Fourier maps were calculated for the refined models in space group $R3\bar{m}$ for sample S1 at 1.9 K and for sample S3 at 2 K, see Fig. 7 in the Appendix, using the software JANA2006. The maps show the nuclear scattering density within the unit cell. If an atom is missing in the refinement, there should be an additional peak at this position. All atoms of Bi$_2$Se$_3$ are clearly visible but no other features appear in the Fourier maps. Shallow peaks like the one at (1/3, 2/3, 0.025) appearing vertically displaced from occupied positions might point to some occupational mixing or insufficient treatment of the atomic displacements. The Fourier maps thus do not indicate the location of the extra Cu ions, and in particular they confirm the absence of a significant amount of Cu at (0, 0, 1/2).

With the precise $c$ lattice parameters determined by our X-ray diffraction experiment and with the structural parameters of reference 23 we can compare the width of the van-der-Waals gap, which amounts to 2.532(4) Å for the parent compound. For the doped compound, we use the average of the $z$ parameter of Se3 determined at 300 K and obtain 2.565(2) Å. The enhancement of the $c$ lattice parameter is thus realized by an increase of the van-der-Waals gap giving support to the idea that Cu ions are inserted in this gap.

It is thus not possible to detect the position of the inserted Cu with our comprehensive diffraction experiments. At the initially proposed intercalation position and at Cu (v) no Cu can be detected at all, and also the other positions Cu (i) to (iv) only yield a total contribution of 0.036(10) for $x$ in the formula Cu$_x$Bi$_2$Se$_3$ while $x \sim 0.3$ is expected. We must conclude that the Cu atoms do not occupy a well defined position in Cu$_x$Bi$_2$Se$_3$, which otherwise would have been detected in the Fourier maps. Instead there must be some positional smearing, which results in very large atomic displacement parameters impairing the detection of the dopant by diffraction. Part of this positional smearing can stem from the separation of superconducting and non-superconducting regions that should differ in their Cu content in the distribution of the dopants in the lattice. The ill-defined dopant position can furthermore be the consequence of clustering.

2. Structural phase transition and monoclinic distortion

If a structural phase transition occurs between room and low temperature, one expects some anomalies in the temperature dependence of fundamental Bragg peaks as well. The intensities of three different reflections and their equivalents in space group $R3\bar{m}$ were followed upon cooling, see Fig. 4. The integrated intensities of most equivalent reflections agree even at low temperature, and there is no anomaly visible in the temperature dependencies of the integrated intensities, which reflect the smaller atomic displacement parameters at low temperature. That there is an enhanced temperature dependence in the reflections (4 1 15) and equivalent ones most likely arises from the different temperature dependencies of the quintuple layers and the van-der-Waals gaps, but again there is no evidence for a structural phase transition. Also the width of the reflections do not yield any indication for structural phase transition, as the peak profiles that are shown for three reflections in the lower panels of Fig. 4 do not change. These temperature-dependent data were taken with $\omega$ scans and a two-dimensional detector resulting in three-dimensional data sets for each Bragg peak at each temperature. We have numerically analyzed the resemblance of these three-dimensional data taken at different temperatures for an individual Bragg peak, see Fig. 6 in the Appendix. This procedure would also detect some anomaly in the mosaic spread due to twining,
structural distortion is described by an irreducible representation at the Γ point of the Brillouin zone. There are only two isotropy subgroups of $R\overline{3}m$ that are centrosymmetric and break the threefold rotation axis, $C2/m$ and $R\overline{3}m$. The same conclusion was also drawn for Sr-doped Bi$_2$Se$_3$. However, the symmetry can be lower than $R\overline{3}m$ and keep the full translation symmetry, which means that the structural distortion is described by an irreducible representation at the Γ point of the Brillouin zone. There are only two isotropy subgroups of $R\overline{3}m$ that are centrosymmetric and break the threefold rotation axis, $C2/m$ and $R\overline{3}m$.

but there is no indication for any anomaly in this resemblance analysis. The absence of a structural phase transition agrees with specific-heat measurements indicating a smooth temperature dependence for Sr-doped Bi$_2$Se$_3$. The same conclusion was also drawn for Sr-doped Bi$_2$Se$_3$.

Breaking of translation symmetry can give rise to superstructure reflections that are forbidden in space group $R\overline{3}m$ and break the general selection rule $-h+k+l=3n$. 152 such forbidden reflections were collected at 300 K and 167 at 1.9 K with sample S1. If these reflections are absent, it is expected that ~68% of the experimental values lie within one standard deviation away from 0. More specifically: The quotient $\frac{\sum I}{\sum \sigma}$ of the intensity divided by its error should exhibit a Gauss distribution with mean value 0 and standard deviation 1. For a few forbidden reflections, a neighboring strong Bragg reflection induces significant intensity, but inspection of the three-dimensional data shows an off-centering and thus a contamination of neighboring Bragg peaks due to the long $c$ axis. After excluding such contaminated reflections the entity of the normalized forbidden intensities exhibits the expected Gauss distribution centered at zero with width one; therefore we can exclude a significant breaking of the translational symmetry in Cu$_2$Bi$_2$Se$_3$. The same conclusion was also drawn for Sr-doped Bi$_2$Se$_3$.

However, the symmetry can be lower than $R\overline{3}m$ and keep the full translation symmetry, which means that the structural distortion is described by an irreducible representation at the Γ point of the Brillouin zone. There are only two isotropy subgroups of $R\overline{3}m$ that are centrosymmetric and break the threefold rotation axis, $C2/m$ and $R\overline{3}m$. The same conclusion was also drawn for Sr-doped Bi$_2$Se$_3$.

and these two only differ in the image of the multidimensional order parameter. Therefore, we may restrict the analysis to the simpler one, $C2/m$, but need to take twinning into account. The monoclinic lattice results from the rhombohedral one by $a' = -2/3a - 1/3b + 2/3c$, $b' = -b$ and $c' = 2/3a + 1/3b + 1/3c$ without a shift of the origin. Note that the primitive lattices are identical for $R\overline{3}m$ and $C2/m$ and there no additional selection rules.

In space group $C2/m$, as in $R\overline{3}m$, there are also three inequivalent sites, Bi1, Se2 and Se3, and compared to the high-symmetry refinement, there are only two additional position parameters, an in-plane displacement for Bi1 and for Se3. For the description of the atomic displacement parameters we keep the constraints from space group $R\overline{3}m$: $U_{11}=U_{22}$, $U_{13}=U_{23}=0$ and $U_{12}=2U_{11}$. Therefore the refinement in space group $C2/m$ adds only four additional parameters (two position parameters and two twin fractions). We can compare the reliability factors of the $C2/m$ refinements with those obtained in $R\overline{3}m$ by describing the high symmetry phase in the low-symmetry setting. As can be seen in Table V in the Appendix, for the three refinements there is a significant improvement in all reliability factors that is also reflected in a reduction of the goodness of fit values. Note that the $R\overline{3}m$ and $C2/m$ refinements cannot be directly compared, because in the former case the data set is much smaller by merging many equivalent reflections.

Further support for the symmetry reduction is given by the good agreement of the five different refinements. We always find a significant displacement of the Bi positions...
while the Se3 ion stays at the high symmetry position as shown in Table [11]. The Bi displacement is illustrated in Fig. 5. The twin fractions indicate an almost equal occupation of the three twin orientations in the two large crystals studied here. Note, however, that the monoclinic distortion of the translation lattice is too small to be detected with the resolution of the single-crystal neutron diffraction experiment.

In spite of its weakness the structural distortion can be essential for the observation of a large anisotropy in the nematic superconducting state by polling the superconducting domains similar to the case of Cu1.5(PbSe)5(Bi2Se3)6 where the nematic axis follows an intrinsic structural symmetry breaking[20]. The monoclinic distortion is the natural candidate to generate the uniaxial strain discussed by Venderbos et al.[31] to lift the degeneracy of the two superconducting components. The nematic superconducting transition exhibits an improper ferroelastic character and can thus be efficiently poled by small strain.

Evidence for a structural distortion was obtained also for Sr-doped Bi2Se3 by high resolution X-ray experiments at room temperature[24] and by a tiny anomaly in the thermal expansion occurring slightly above the superconducting transition in a Nb doped sample[22]. In both cases the structural distortion are well below the resolution in our experiments. But qualitatively the room-temperature distortion reported for the Sr system[12] corresponds to our finding of a monoclinic space group for Cu doping.

Further support for the reliability of these structural refinements can be obtained from the anisotropic displacement parameters given in Table V in the Appendix. The small displacement of the Bi atom is visible in a minor reduction of the Bi U11 parameter in space group C2/m. In general there is a strong anisotropy of the displacement parameters with U33 > U11, which can be explained by the layered character of the Cu2Bi2Se3 structure that exhibits strong bonding only within the quintuple layers. Therefore, c polarized phonons must be much softer and imply large U33 values.

In the high-symmetry space group R3m, there are two different Bi − Se distances: One from Bi to the Se atom at the border of the van-der-Waals gap and another one to the Se in the middle of the quintuple layer. These two distances amount to 2.8642(25) Å and 3.0745(23) Å, respectively. We use the c parameters obtained on our crystals, the in-plane lattice parameter from reference[27] and the structural parameters are averaged from refinements of the data collected at 1.9 K and 2 K. In the low-symmetry space group C2/m, each of these two distances splits into two different ones, see Fig. 5. The distance from the Bi atom to one of the border Se atoms amounts to 2.8381(28) Å and the distances to the other two Se atoms at the border are 2.8769(26) Å. The other distance splits into 3.0980(24) Å (occurring once) and two 3.0635(23) Å distances. Already in the high-symmetry phase the Bi atom is not situated at the center of the surrounding octahedron but moves towards the border of the quintuple layer. In Bi2Se3, Bi shows a formal 3+ valence state, which typically exhibits lone-pair behavior[32–34]. For Bi3+, there is a pair of electrons outside the filled Xe shell, whose probability density can deviate from spherical symmetry. The strong off centering in the high-symmetry structure can already be related with such an effect. The structural symmetry-breaking displacement in the low-symmetry phase C2/m allows for horizontal offcentering of the lone-pair electron distribution.

If one admits a loss of inversion symmetry, the low-symmetry phase breaking the rotational axis without a loss of translation symmetry corresponds to space group Cm[27]. Note, however, that there is no evidence of broken inversion symmetry so far. Describing the structure in Cm requires 13 additional structural parameters and at least two twin parameters. We have refined this structural model with all 5 data sets, but we do not obtain evidence for such a distortion. The large number of additional parameters combined with the twinning impairs a reliable refinement.

IV. CONCLUSIONS

Our comprehensive neutron diffraction studies on superconducting single crystals of Cu1−xBi2Se3 with x ~ 0.3 show that the dopant is not simply occupying the central intercalation position, but also at other proposed sites we do not detect significant amounts of Cu. The position of the Cu ion remains a mystery, but the enhanced thickness of the van-der-Waals gap supports the idea of intercalation between the layers. For any Cu incorporated in the Bi2Se3 structure, we assume considerable disorder arising from clustering to hide it in diffraction studies. We also do not find any evidence for a structural phase transition occurring between room temperature and the superconducting phase similar to caloric studies. However, the five collected Bragg reflection data sets consistently indicate a weak structural distortion lowering the symmetry to the monoclinic space group C2/m. This monoclinic distortion can be related to the lone electron pair of the Bi and be essential for the analysis of the nematic superconductivity in doped Bi2Se3 in spite of its weakness.

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V. APPENDIX

A. Additional information about the refinements

In table III, we compare the reliability factors of refinements in space group \( R\bar{3}m \) with empty, full and partially occupied intercalation position at (0 0 1/2). We can exclude a significant Cu occupation of this site.

| Sample: S1 | without Cu \( R_{\text{obs}}(wR_{\text{obs}}) : 3.07(3.55) \) | with Cu \( R_{\text{all}}(wR_{\text{all}}) : 3.71(3.71) \) | free occ(Cu) \( R_{\text{obs}}(wR_{\text{obs}}) : 5.05(5.25) \) | \( R_{\text{all}}(wR_{\text{all}}) : 5.71(5.36) \) | occ(Cu) : −0.006(5) | \( R_{\text{obs}}(wR_{\text{obs}}) : 3.15(4.83) \) | \( R_{\text{all}}(wR_{\text{all}}) : 4.69(5.04) \) | occ(Cu) : 0.000(7) |
|---|---|---|---|---|---|---|---|
| 1.9 K | 12.99(14.48) | 3.07(3.54) | 14.09(14.61) | 3.69(3.70) | −0.006(5) | 15.32(17.29) | 3.15(4.83) | 0.000(7) |
| 4.4 K | 14.51(16.25) | 4.98(5.24) | 15.36(16.34) | 5.74(5.38) | 0.000(7) | 16.92(17.40) | 4.69(5.04) | 0.000(7) |
| 300 K | 15.34(17.64) | 4.98(5.24) | 16.92(17.40) | 4.69(5.04) | 0.000(7) | 15.34(17.64) | 4.98(5.24) | 0.000(7) |

Table IV compares the reliability factors of the refinements in space groups \( R\bar{3}m \) and \( C2/m \). The column below \( R\bar{3}m \) gives the standard values for the high-symmetry refinement, which, however, cannot be directly compared to those in space group \( C2/m \) because data are differently merged. Therefore, we have also described the high-symmetry phase in space group \( C2/m \) by restraining the two extra parameters and by setting fixed domain ratios. This can be directly compared to the refinements in \( C2/m \) as indicated by the arrows. With the five data sets, we obtain a weak but significant reduction of the reliability parameters in agreement with improved goodness of fit values.

The anisotropic displacement parameters obtained in the refinements of the \( R\bar{3}m \) and \( C2/m \) structures with the five data sets are shown in Table V. In both structures, we keep the symmetry constraints of the rhombohedral structure. The displacement parameters are quite anisotropic with larger \( U_{33} \) values, which reflects the layered character of the \( \text{Bi}_{2}\text{Se}_{3} \) crystal structure. Strong bonds only exist within the quintuples layers, while the inter-layer bonding only arises from the van der Waals potential. The refinements indicate soft \( c \) polarized phonons.

| Sample: S1 | \( R_{\text{obs}}(wR_{\text{obs}}) : 3.07(3.55) \) | with Cu \( R_{\text{all}}(wR_{\text{all}}) : 3.71(3.71) \) | GoF = 2.07 | GoF = 1.67 → 1.51 |
|---|---|---|---|---|
| 1.9 K | 3.35(3.69) → 3.07(3.46) | 4.82(4.04) → 4.68(3.62) | 4.82(4.04) → 4.68(3.62) | 4.82(4.04) → 4.68(3.62) |
| 4.4 K | 5.05(5.25) | 4.90(5.33) → 4.78(5.22) | 5.71(5.36) | 6.57(5.69) → 6.38(5.36) |
| 300 K | 4.69(5.04) | 6.32(5.67) → 6.29(5.47) | 2.74 | 2.31 → 2.25 |

Sample: S3

| Sample: S3 | \( R_{\text{obs}}(wR_{\text{obs}}) : 3.12(3.97) \) | with Cu \( R_{\text{all}}(wR_{\text{all}}) : 3.24(3.99) \) | GoF = 2.77 | GoF = 2.16 → 1.90 |
|---|---|---|---|---|
| 2 K | 3.41(3.99) → 2.96(3.52) | 4.14(4.14) → 3.79(3.60) | 4.14(4.14) → 3.79(3.60) | 4.14(4.14) → 3.79(3.60) |
| 300 K | 4.83(5.11) | 5.83(6.50) → 5.68(5.03) | 3.26 | 2.55 → 2.32 |

Table V. Refinements in space group \( R\bar{3}m \) and \( C2/m \) for different samples and temperatures. In order to compare the reliability values, the refinements in space group \( C2/m \) were carried out with the same structural parameters as in \( R\bar{3}m \) (left of the arrow \( \rightarrow \)) and then with the structural parameters refined according to space group \( C2/m \) (right of the arrow \( \rightarrow \)). The \( wR(\text{all}) \) values improve by approximately 0.5%, all reliability values are given in % .

B. Analysis of the resemblance of Bragg scattering data

We have analyzed the resemblance of Bragg scattering data taken as function of temperature by calculating the correlation function for data taken at temperatures \( T_1 \) and \( T_2 \) as

\[
r(T_1, T_2) = \frac{I_1 I_2 - I_{T1}^2 I_{T2}^2}{\sqrt{(I_{T1}^2 - I_{T1}^2)^2 (I_{T2}^2 - I_{T2}^2)}}
\]

where \( I_T \) is the number of counts at temperature \( T \) and the vinculum denotes the mean with respect to all pixels and \( \omega \) positions.

The correlation function defined in equation (1) does not depend on the total intensity of the signal, but only on the distribution along the \( \omega \) scan and the pixels. If the peak shape or position differ at two temperatures \( T_1 \) and \( T_2 \), the quantity \( r(T_1, T_2) \) is small.

In Fig. 6 we show colour maps of the \( r(T_1, T_2) \) values plotted against the two temperatures. It can be seen that there is a strong tendency that the detector images are similar for similar temperatures and differ more strongly if the temperature difference is greater. If the detector images changed suddenly, there would be two temperature intervals, where correlation coefficients are high for temperatures that lie in the same interval and lower correlation coefficients for temperatures in different inter-
TABLE VI. Anisotropic displacement parameters of the atoms of Bi$_2$Se$_3$ of the samples S1 and S3 at different temperatures refined in space groups $R\overline{3}m$ and $C2/m$. The constraints for ADPs in space group $R\overline{3}m$, $U_{11} = U_{22} = 2U_{12}$ and $U_{13} = U_{23} = 0$ are also used in $C2/m$, and all parameters are given in 10$^{-4}$Å$^2$.

| Sample: S1 | $R\overline{3}m$ | $C2/m$ |
|------------|-----------------|---------|
| Bi1        | 42(4)           | 29(3)   |
| Se2        | 45(5)           | 27(5)   |
| Se3        | 39(4)           | 43(4)   |
| 1.9 K      | 97(5)           | 76(4)   |
| Se2        | 95(6)           | 73(6)   |
| Se3        | 99(5)           | 97(5)   |
| 4.4 K      | 155(7)          | 141(5)  |
| Se2        | 132(9)          | 122(9)  |
| Se3        | 147(8)          | 147(8)  |

| Sample: S3 | $R\overline{3}m$ |
|------------|-----------------|
| Bi1        | 13(4)           |
| Se2        | 10(4)           |
| Se3        | 16(4)           |
| 2 K        | 83(7)           |
| Se2        | 68(9)           |
| Se3        | 77(8)           |
| 300 K      | 83(7)           |
| Se2        | 68(9)           |
| Se3        | 77(8)           |

C. Calculated scattering density maps

Extra scattering arising from the inserted atoms can be visualized in the scattering maps obtained by Fourier transformation. Such calculated maps are shown in Fig. 7 for Bragg reflection data taken with sample S1 at 1.9 K. However, there is no evidence for extra scattering in these maps, which only show the expected peaks at the Bi and Se positions. Fourier maps calculated for the other sample S3 at 2 K also do not indicate extra scattering.

FIG. 6. Color maps of the correlation function of the Bragg scattering data taken at two sets of equivalent reflections; the correlation function is plotted against the two temperatures to be compared. For all reflections there is no indication for a discontinuity of the correlation function as it is expected for a structural phase transition.

FIG. 7. Total scattering maps calculated with data set taken on sample S1 at 1.9 K. The Bi and Se atoms are clearly visible, but there is no evidence for any extra scattering in these maps.

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