Experimental report

10/09/2019

Proposal: 5-11-426 **Council:** 4/2018

Title: Structure determination of the possibly topological superconductor CuxBi2Se3

Research area: Physics

This proposal is a continuation of 5-41-914

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Samples: CuxBi2Se3

Instrument	Requested days	Allocated days	From	To
D9	7	7	04/07/2018	06/07/2018
			14/09/2018	20/09/2018

Abstract:

The crystal structure of CuxBi2Se3 - possibly a topological superconductor with spin triplet pairing - is not unambiguously determined so far. Substantial progress could be achieved by the experiment 5-41-914 carried out in 2017 on D9 suggesting a fully different interpretation with a symmetry breaking already in the normal state of Cu doped Bi2Se3. A precise knowledge of the crystal structure in all relevant temperature regimes provides the basis for understanding this material including it possibly topological superconductivity.

Structure determination of the possible topological superconductor $Cu_xBi_2Se_3$

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The compound Bi_2Se_3 with space group R-3m is a topological insulator [1] and Cu doping induces superconductivity below a transition temperature of T_c = 3.8 K [2]. Several experiments reveal a breaking of the three-fold symmetry [3-9] for the Cu-doped compound in the superconducting phase.
The Cu intercalation was described by an occupation of the van-der-Waals gaps between neighbored Se layers by Cu atoms which was confirmed by X-ray diffraction [2]. However, during the beam time 5-41-914 on D9, we could not detect any hint for Cu atoms occupying these sites. Furthermore, we found some hints for a breaking of the three-fold axis, which however are not sufficient to unambiguously identify this symmetry reduction. This is why we proposed another beam time on this compound in order to investigate the crystal structure of $Cu_xBi_2Se_3$.

Structural refinements with Se vacancies were carried out. Such vacancies can be excluded with a precision in the order of magnitude 1 %. By this result, also a statistical occupation of Bi sites with Cu atoms can be excluded, however the uncertainty is about 10 % due to very similar scattering lengths of Se and Cu nuclei. So, it is possible that a small amount of Cu is indeed present at these sites.

Refinements with Cu atoms at the position 3b (0, 0, 1/2) as claimed in [2] were carried out. When the occupation of these sites is refined, in all cases the result is consistent with zero. Thus, in accordance with our earlier investigations, no intercalated Cu atoms at these positions can be detected.

Theoretical simulations in [10] propose five further possible positions for the Cu atoms. Refinements with Cu occupying all these possibilities were carried out. All of them yield occupancy values below 1 %, most of them compatible with zero within one standard deviation. So there is no evidence for any of these positions to be significantly occupied by the dopant.

Temperature-dependent scans of equivalent reflections are supposed to show the breaking of the three-fold axis. No such phase transition is visible as depicted in Fig. 1.

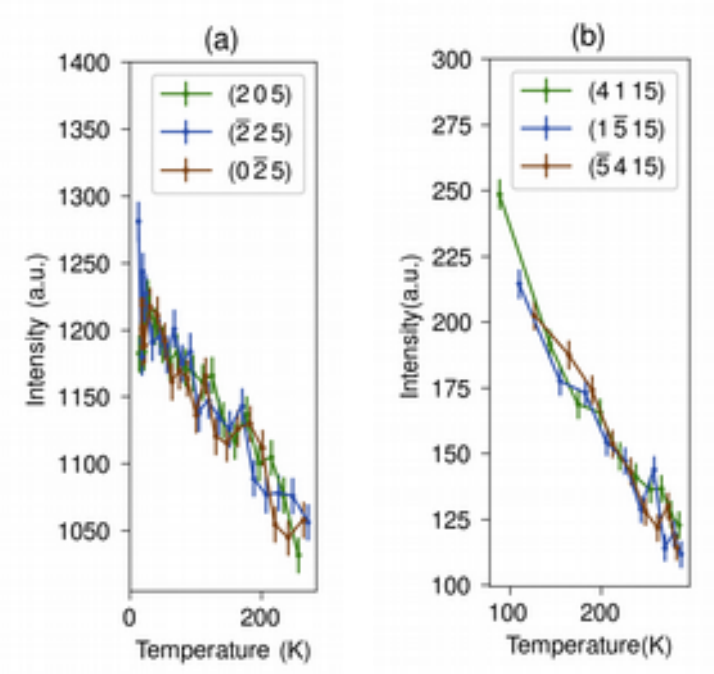

Fig. 1: Temperature scans of the reflections (2 0 5) (a), (4, 1, 15) (b) and equivalent reflections. No clear indication for a structural phase transition is visible.

Also a breaking of the rhombohedral centering was investigated by searching for reflections that violate the selection rule -h + k + l = 3n. The statistical distribution of these reflections is in good agreement with a Gaussian distribution around zero. Outliers can be explained by artifacts caused by neighbored strong reflections. Thus, the rhombohedral centering is not broken.

Refinements in space group C2/m yield better R values compared to refinements in space group R-3m if the data reduction is carried out like in C2/m. In order to directly compare the refinements in the R-3m and C2/m the parent structure was described in C2/m by constraining the positions to the high symmetry positions. In total there are 5 different data collections with two samples from different badges. For all analyses we yield slightly better R-values with C2/m distortion at the border of statistical significance. However, the structural displacements for the 5 data sets agree well to each other. There is only a significant displacement for the Bi atoms while Se positions stay within the errors at the high symmetry positions. The displacement of the Bi atoms are though quite small of the order of 0.05Å, therefore there is only a weak impact on ADP's which are slightly smaller in the C2/m treatment. The main distortion is a shift of the Bi atoms inside the a-b plane away from the centers of the [$BiSe_6$] octahedrons as depicted in Fig. 2 and is reminiscent of an out-of-center position of a Bi ion due to lone pairs.

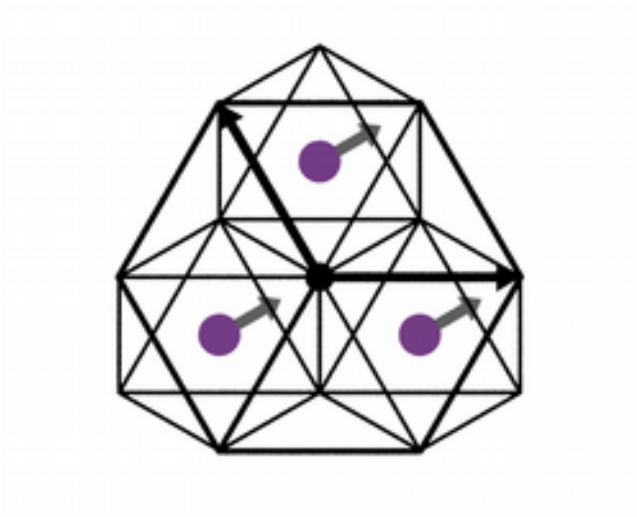

Fig. 2: Structural deviation of the Bi atoms in space group C2/m. The arrows indicate the shift, enlarged by a factor of 50.

It can be concluded that no Cu is present at the 3b (0, 0, 1/2) position in superconducting $Cu_xBi_2Se_3$ contrary to what is proposed in reference [2]. Also at the positions proposed in reference [11] no Cu could be detected. A substitution occupation of the Bi sites by Cu can be ruled out only with a precision of 10 %. We found no hint for a structural phase transition by temperature scans of equivalent reflections. Refinements in the lower-symmetry space group C2/m suggest small structural distortions at the border of statistical significance. In this distortion there is a slight shift of the Bi atoms away from the center of the $BiSe_6$ octahedrons.

[1] Y. Xia et al. Nature Physics **5** (2009), pp. 398-402. [2] Y. S. Hor et al., Physical Review Letters **104** (2010), p. 057001. [3] K. Matano et al., Nature Physics **12** (2016), pp. 852-855. [4] T. Asaba et al., Phys. Rev. X **7**, 011009 (2017). [5] S. Yonezawa, et al. Nature Physics **13**, 123 (2017). [6] Y. Pan, et al. Sci. Rep., **6**, 28632 (2016). [7] G. Du, et al. Sci. China Phys., Mech. & Astr., **60**, 037411 (2017). [8] J. Shen, et al., npj Quant. Mat. **2:59** (2017). [9] M. P. Smylie, et al., arXiv:1712.03215. [10] Y.-L. Wang et al., Phys. Rev. B **84**, 075335 (2011). [11] S. Nakajima, J. Phys. Chem. Solids **24** (1963), pp. 479-485.