Experimental report

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Title: Structure determination of the possibly topological superconductor CuxBi2Se3

Research area: Physics

This proposal is a new proposal

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Samples: Cu0.32Bi2Se3

Instrument	Requested days	Allocated days	From	To
D9	10	10	17/02/2017	27/02/2017

Abstract:

CuxBi2Se3 is a promising candidate for being a topological superconductor with spin triplet pairing. Theoretically, it fulfills a sufficient criterion for this, and also experimentally there are several evidences for spin triplet pairing. However, the crystal structure is still not solved in detail. Especially the position of the Cu-atoms is not known. The Cu-doping plays an important role for superconductivity.

Structure determination of the possibly topological superconductor $Cu_xBi_2Se_3$

Topological superconductors, which are closely related to topological insulators [1], exhibit gapless surface Andreev bound states while the bulk is fully gapped [2]. Cu-intercaletad Bi_2Se_3 is of special interest, because there are theoretical indications that it might be a realization of a spin-triplet-pairing topological superconductor [2]. Undoped Bi_2Se_3 is known to be a topological insulator [3] and it indeed could be experimentally shown that Cu intercalation induces superconductivity below the transition temperature of 3.8 K [4]. Bi_2Se_3 is a strongly two-dimensional material consisting of weakly coupled double-layers of $BiSe_6$ octahedrons. The crystals used in this experiment were provided by the group of Prof. Ando at Cologne University.
Since magnetic fields are shielded by the Meissner effect, spin triplet pairing cannot be detected by standard susceptibility measurements. However, a measurement of the Knight shift reveals a two-fold symmetry deep in the superconducting phase, which is a hint for a breaking of the spin-rotation symmetry [5]. Magnetic neutron scattering on D3 (5-51-508) reveals magnetic moments in the superconducting state, however their temperature dependence does not correspond to that expected for triplet pairing. Therefore, the origin of these moments remains quite unclear.
The precise crystal structure of Cu-intercalated $Cu_xBi_2Se_3$ is still unknown because of the mechanical instability of the material. Single crystals of Bi_2Se_3 and of Cu-doped Bi_2Se_3 are extremely difficult to handle due to the strong two-dimensional nature of the crystal structure. Therefore, any attempts to prepare a sample for X-ray structure analysis out of the as-grown crystals failed, and only powder X-ray diffraction analysis is reported, which also suffers from the unfavorable real structure. One aim of the present experiment was therefore to use a larger as-grown superconducting sample with neutron diffraction to establish reliable structural data. Especially there was no unambiguous determination of the Cu positions. It is usually assumed that the Cu ions intercalate between the layers of Bi_2Se_3 [4]. It seems natural that the Cu ions are located at the position $(0, 0, 1/2)$.
We collected 592/5859/530 reflections, of which 182/203/157 are unique at 1.9/4.4/300 K, respectively, in a 2-stage Displex with an additional Joule-Thompson stage. Three refinements were carried out using the Bi_2Se_3 structure without Cu intercalation, a Cu occupation of 0.3 corresponding to the stoichiometry of the sample, and a variable occupation of the Cu sites, respectively. The results for 1.9 K are listed in Table 1. The definitions of the different R values are given in [6]. A high value indicates a bad fit between the model and the measured data, while a good refinement should typically yield values below 3 %. It can be seen from Table 1 that the model without Cu intercalation yields good R values, whereas the R values worsen drastically when the Cu ions are included to the model. A refinement of the Cu occupation yields slightly negative occupation values and nearly the same R values compared to the Cu-free model.
This result is a clear evidence, that the Cu atoms are not entering the crystal structure at the position previously assumed. Also attempts with further models, including the Cu ions at different positions, could not significantly improve the R values. Besides this uncertainty, the structure refinement resulted in satisfyingly precise structure parameters.
A further issue is, whether the three-fold rotation symmetry is broken, as suggested by the previously mentioned Knight shift measurement [5]. A breaking of the three-fold symmetry would lead to space group $C2/m$ or lower, in which the Bi site is split into three different symmetrically not equivalent sites. We carried out refienements of the diffraction data at all three temperatures in space group $C2/m$. In order to avoid over-parametrization, atomic displacement parameters (ADPs) are assumed to be isotropic. Furthermore, the occupation of the Bi sites is refined, which models an occupation of the Bi sites by Se or Cu atoms which have a coherent scattering length of 7.970 fm / 7.718 fm compared to 8.532 fm for Cu. The strongest

indication for a lower symmetry is the improvement of the internal R value (upon averaging) by 3.18 % → 1.55 % / 3.88 % → 2.60 % / 4.45 % → 1.17 % for the three temperatures, respectively. Table 2 shows the results of these refinements. It can be seen, that at all three temperatures, the site Bi1_3 has a smaller occupancy than the other two. This is an indication for a substitution by Se or Cu on this site. The symmetry reduction is also visible in a strong variation of the Bi-Se distances among the three sites.
A few days of beamtime were lost due to problems with the alignment of the incoming beam on the sample. While the atomic positions at 1.9 K and 4.4 K in $C2/m$ yield very similar values, the distortion at 300 K seems to be different. However, the data at 300 K were collected before the beam was readjusted. So we cannot unambiguously decide whether the structural difference is a temperature-dependent effect or just an artefact.

	without Cu	stoichiometric occupation	variable occupation
R(obs)	3.09 %	13.59 %	3.08 %
wR(obs)	3.57 %	15.09 %	3.56 %
R(all)	3.69 %	14.64 %	3.67 %
wR(all)	3.72 %	15.21 %	3.70 %

Table 1: R values of refinements for different structure models in space group $R\bar{3}m$ of $Cu_xBi_2Se_3$, explained in the text.

	1.9 K	4.4 K	300 K
R(obs)	2.93 %	4.88 %	3.91 %
wR(obs)	3.23 %	6.05 %	4.68 %
R(all)	4.46 %	6.03 %	14.02 %
wR(all)	3.38 %	6.15 %	6.05 %
occupation Bi1_1	1.0(2)	1.19(10)	1.07(3)
occupation Bi1_2	1.09(15)	1.04(12)	1.25(3)
occupation Bi1_3	0.93(17)	0.79(10)	0.69(3)

Table 2: Refinements in space group $C2/m$ with variable occupation of the three non-equivalent Bi sites. An occupation smaller than 1 indicates a substitution by Se or Cu.

[1] Y. Ando. "Topological Insulator Materials". In: *Journal of the Physical Society of Japan* **82** (2013), p. 102001.

[2] L. Fu and E. Berg. "Odd-Parity Topological Superconductors: Theory and Application to $Cu_xBi_2Se_3$". In: *Physical Review Letters* **105** (2010), p. 097001.

[3] Y. Xia et al. "Observation of a large-gap topological-insulator class with a single Dirac cone on the surface". In: *Nature Physics* **5** (2009), pp. 398–402.

[4] Y. S. Hor et al. "Superconductivity in $Cu_xBi_2Se_3$ and its Implications for Pairing in the Undoped Topological Insulator". In: *Physical Review Letters* **104** (2010), p. 057001.

[5] K. Matano et al. "Spin-rotation symmetry breaking in the superconducting state of $Cu_xBi_2Se_3$". In: *Nature Physics* **12** (2016), pp. 852–855.

[6] P. A. Karplus and K. Diederichs. "Linking crystallographic model and data quality". In: *Science* **336** (2012), pp. 1030–1033.