Experimental report

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Proposal: 5-14-272 **Council:** 10/2019

Title: Crystal structure determination ofthe topological and nematic superconductor SrxBi2Se3

Research area: Physics

This proposal is a new proposal

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Experimental team: Alexandre BERTIN

Local contacts: Nebil AYAPE KATCHO

Samples: Sr_xBi2Se3

Instrument	Requested days	Allocated days	From	To
IN3	1	1	07/09/2020	08/09/2020
D9	7	7	21/09/2020	28/09/2020

Abstract:

Doping Cu, Nb or Sr into the topological insulator Bi2Se3 results in superconducting states that are proposed to be topological as well. The superconducting properties in all three materials break the threefold rotation axis of the parent compound pointing to a nematic state. In spite of these highly interesting superconducting states very little is known about the crystal structure of these materials, because samples for X-ray studies could not be cut. Our previous neutron single-crystal experiment on the Cu-doped material showed that Cu is not intercalating and gave weak evidence for a structural distortion already in the normal state. We propose to analyse the crystal structure for another dopant, Sr, to support our conclusions for this important class of materials.

Experimental Report

Instrument	D9
Proposal Number	5-14-272
Proposal	Crystal structure determination of the topological and nematic superconductor $Sr_xBi_2Se_3$
Experimentalist	Alexandre Bertin, Markus Braden
Local Contact	Nebil Ayape Katcho, Oscar Fabelo Rosa, Anne Stunault

Topological superconductivity (SC) is of great interest because it might provide a realization of quantum computers [1]. Like topological insulators [2], topological superconductors (SC) are fully gapped in the bulk, but they additionally have gapless surface Andreev bound states [3]. The undoped compound Bi_2Se_3 is a topological insulator [4], and Cu doping induces superconductivity below T_c= 3.8K [5]. Inducing Sr or Nb into the Bi_2Se_3 structure has also been established to yield superconductivity. Several experiments in the SC state reveal a lower symmetry suggesting a nematic character [6-12], in which the threefold rotation axis of the parent material would be broken. However, a full understanding of the doped-Bi_2Se_3 structure is still lacking. Even the doping concentration remains unclear. Indeed, because of the layered crystal structure, these crystals cannot be cut without destroying them, hampering a full structural analysis with conventional single-crystal X-ray diffraction. Recent single-crystal neutron diffraction studies of $Cu_xBi_2Se_3$ could not unambiguously resolve the Cu atomic position, and no structural transition has been identified. Only a slight monoclinic distortion has been evidenced, but does not change across the superconducting transition, and thus cannot be associated to the nematic phase [13].

In order to complement the structural knowledge of doped-Bi_2Se_3 compounds, single-crystal neutron diffraction experiments have been performed on D9 with a different type of doping: $Sr_xBi_2Se_3$. Sr-doped single crystals were grown in the group of Prof. Ando (Univ. Cologne) and exhibit a rectangular plate-like shape of 3mm x 4mm and thickness between 0.5mm and 1mm. The superconducting transition is found to be T_c= 2.8K, with a shielding fraction of about 40% at 1.8K and close to 100% at 0.3K. The pristine compound Bi_2Se_3 crystallizes in space group R-3m with lattice constants a = b = 4.14Å and c = 28.64Å (hexagonal setting) [5].

Reflections were collected at three different temperatures: 1.8K, 3.9K, and 300K, see Tab.1. At 1.8K and 300K, not only reflections belonging to *R-3m* but also to P1 were collected, in order to look for superstructure reflections. However, the broad mosaicity due to the layered structure along the *c* axis may lead to a contamination from an intense neighbouring Bragg peak hindering a proper integration of the reflections. Therefore, preliminary refinements at 1.8K only include reflections belonging to *R-3m*.

	T=300K	T=3.8K	T=1.8K
Total	701	691	607
Unique R-3m	251	238	243
Observed R-3m	196	212	186
Unique C2/m	679	668	584
Observed C2/m	513	569	454

Tab.1: Total number of reflections recorded at each temperature, unique reflections after data merging in the corresponding space group, and observed reflections fulfilling the criterion I/σ>3.

The first aim of this experiment was to clarify the Sr atomic position in the crystal structure. Several refinements of the room temperature data set have been carried out using the space group *R-3m*, and the corresponding *R*-values are reported in Tab.2. The two obverse/reverse twins inherent to the rhombohedral structure have been included, but the volume fraction of the reverse twin is found to be 0 within the error bars. Thus, the sample does not exhibit twinning. Refinement (a) is performed without any Sr, refinement (b) includes Sr atoms in the Van der Waals gap at the intercalation position (0 0 1/2), and refinement (c) takes into account the substitution of Bi atoms by Sr atoms. Anisotropic atomic displacement parameters (ADPs) are included for Bi and Se atoms, while fixed isotropic U=0.005Å^2 is used for Sr in refinement (b), and anisotropic ADPs of Sr are fixed to those of Bi in refinement (c). The Sr occupation is found to be 1.3(8)% and 3(6)% for refinement (b) and (c), respectively. Therefore, within the statistical errors, the Sr occupation does not deviate from 0. Thus, the Sr could not be detected at the Bi sites nor at the intercalation position, supporting the conclusions of Ref.[14] and similarly to the results of $Cu_xBi_2Se_3$ structural analysis [13]. Following Refs. [14,15], the Sr atoms could be located in the interstitial sites within the quintuple Bi-Se layers, and further analysis is required to clarify this issue.

	Ref. (a)	Ref. (b)	Ref. (c)
R-values	R_{obs}=8.80, wR_{obs}=8.44 R_{all}=10.72, wR_{all}=8.55 GOF=4.20	R_{obs}=8.77, wR_{obs}=8.39 R_{all}=10.76, wR_{all}=8.50 GOF=4.19	R_{obs}=8.80, wR_{obs}=8.44 R_{all}=10.72, wR_{all}=8.55 GOF=4.2

Tab.2: Reliability factors of room temperature data refinements with the R-3m space group, looking for the Sr atomic position.

The second part of this experiment aimed to investigate the structural distortion breaking the threefold rotation axis and leading to the nematic state. The temperature dependence of the integrated intensities of three set of equivalent reflections in *R-3m* is reported in Fig.1. No anomaly indicative of a structural phase transition could be detected. A breaking of the three fold symmetry axis without breaking the translational or inversion symmetries would lead to the isotropy subgroup *C2/m*. Refinement were carried out in both space groups *R-3m* and *C2/m*, without including Sr atoms, at the three temperatures T=1.8K, 3.8K, and 300K. The three twins inherent to the symmetry lowering have been taken into account. Since the reliability of both refinement cannot directly be compared due to different reflections merging in each space group, a refinement with the *C2/m* space group with structural parameters constrained to those deduced from the high symmetry *R-3m* space group refinement has also been performed, where only the *C2/m* symmetry allowed ADPs and twinning volumes are refined. The reliability factors are shown in Tab.3. The absence of a clear improvement of the *R*-values between the constrained and unconstrained refinements with the *C2/m* space group does not allow us to conclude on the presence of a monoclinic distortion at low temperature.

	R-3m	*C2/m* (constr.)	*C2/m*
T=300K	R_{obs}=8.80, wR_{obs}=8.44 R_{all}=10.72, wR_{all}=8.55 GOF=4.20	R_{obs}=7.49, wR_{obs}=8.21 R_{all}=10.28, wR_{all}=8.33 GOF=3.63	R_{obs}=7.46, wR_{obs}=8.13 R_{all}=10.45, wR_{all}=8.23 GOF=3.59
T=3.8K	R_{obs}=9.04, wR_{obs}=10.36 R_{all}=11.51, wR_{all}=10.63 GOF=6.18	R_{obs}=7.71, wR_{obs}=8.76 R_{all}=10.61, wR_{all}=9.08 GOF=4.60	R_{obs}=7.28, wR_{obs}=8.38 R_{all}=9.74, wR_{all}=8.56 GOF=4.35
T=1.8K	R_{obs}=9.73, wR_{obs}=11.14 R_{all}=12.92, wR_{all}=11.31 GOF=6.20	R_{obs}=8.90, wR_{obs}=9.68 R_{all}=13.12, wR_{all}=10.02 GOF=4.99	R_{obs}=8.61, wR_{obs}=9.50 R_{all}=12.63, wR_{all}=9.80 GOF=4.90

Tab.3: Reliability factors of refinement carried on with the R-3m and C2/m space groups at each temperature.

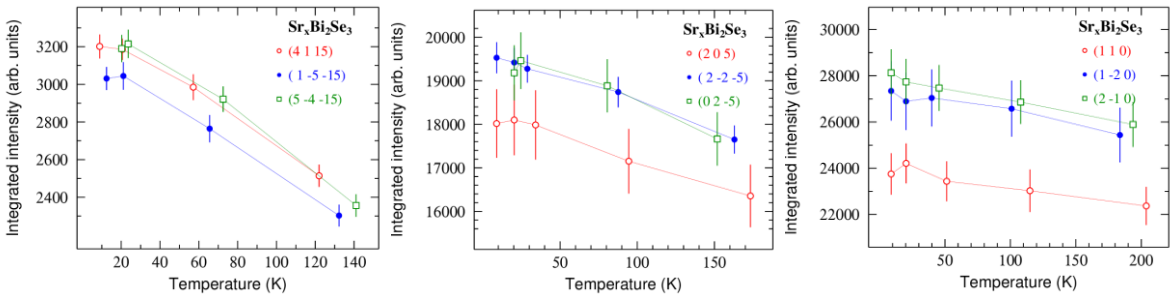

Fig.1: Temperature dependence of the integrated intensities of three set of equivalent reflections in R-3m.

References

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