A New High Pressure form of Ba$_3$NiSb$_2$O$_9$

Local Structure Investigated by Electron Diffraction

X-ray, neutron and electron diffraction methods are widely used for the investigation of crystals. Each of these techniques has their own advantages in terms of element sensitivity, sample size requirements etc. and are chosen accordingly for structure determinations. A less obvious difference lies in the spatial resolution of these diffraction techniques. Here, we show that electron diffraction can elucidate the local structure where X-ray and neutron diffraction only sens the average structure.

Introduction

When spins that interact antiferromagnetically with their neighbors are positioned on a triangular lattice, there is no way that a long range order can satisfy all the interactions. In 1973 Anderson [1] proposed the Quantum Spin Liquid (QSL) state as the ground state for such a system. QSL materials have been widely studied but only few experimental realizations have been achieved. Recently, perovskite related phases Ba$_3$MSb$_2$O$_9$ (M = divalent transition metal) have come into focus [2-6]. In the case of Ba$_3$NiSb$_2$O$_9$ this could lead to a QSL with spin S = 1.

The structure of this compound is built of layers of NiO$_6$ and SbO$_6$ octahedra that are stacked along the c-axis of the hexagonal unit cell. However, there is no agreement in the literature on the way layers are stacked, sharing either corners or faces of the octahedra. Figure 1 shows one of the proposed structures called 6H-A (space group $P6_3/mmc$, $a = 5.8357(2)$ Å and $c = 14.3956(4)$ Å) [7] seen in projection along the a direction (a) and the c direction (b). Note the triangular arrangement of the magnetic Ni$^{2+}$ ions in the ab-planes.

Since this compound does show a long-range magnetic ordering at low temperatures, a new synthesis at 620°C and 2.5 GPa was undertaken in order to obtain a different modification of this phase called 6H-B. In this phase the Ni atoms don’t occupy the same layers as in the 6H-A structure but the upper one of the layers that share octahedron faces.

This still results in a triangular lattice of Ni ions and in a previous study [8] it was reported that this compound presents no magnetic order down to 0.35 K and
suggested that it could be an experimental realization of a gapless QSL.

**X-Ray and Neutron Diffraction**

The sample was first characterized by X-ray powder diffraction (XRPD) with CuK$_{\alpha 1}$ radiation (1.5406 Å) in the 2θ range 10° ~ 90° with a 0.01° step size in order to confirm that no impurity phase was present. In addition we carried out a neutron powder diffraction (NPD) experiment on the two-axis diffractometer D1B at Institut Laue Langevin (ILL, Grenoble, France). The XRPD and NPD data were used to perform a combined Rietveld refinement of the crystal structure [9].

The main goal of the XRPD-NPD experiment was to determine the presence of structural disorder in the cation stacking sequence of the 6H-B samples. Due to the difference in scattering contrasts between atomic species for the two radiations combined refinements using both types of data are expected to yield more accurate results. In particular, the occupancies of the Sb/Ni sites corresponding to the face sharing octahedra were refined with the constraint that each site should be fully occupied. The resulting fits were satisfactory and one major result of the refinement is the observation of a disorder between (Ni$^{2+}$/Sb$^{5+}$) and (Sb$^{5+}$/Ni$^{2+}$) dimers in the double layers of octahedra. The consequences are quite important for the physical properties, since in this case the frustrated magnetic Ni$^{2+}$ triangular planes would no longer exist.

**Electron Diffraction and Z-Contrast Imaging**

In order to get more detailed information about this possible disorder, we investigated the sample using electron diffraction and transmission electron microscopy (TEM) Z-contrast imaging.

An advantage of electron diffraction compared to XRPD and NPD is that the former offers the possibility of obtaining single crystal diffraction data from very small volumes of a sample, i.e. a single particle of a powder. We can therefore avoid peak overlap and compared to XRPD and NPD, precession electron diffraction (PED) can provide insight on the structure at a much more local level.

The PED patterns obtained from very thin particles showed intensity distributions lacking a mirror symmetry perpendicular to the c* direction (fig. 2a). This is incompatible with a 6-fold rotation axis along c* since the 6-fold axis combined to Friedel’s law would lead to a 2mm symmetry of the [0 1 0] zone axis, whereas figure 2a clearly shows only a symmetry 2 without any mirror. This optical impression is corroborated by the profile (fig. 2b) obtained from the boxed area in figure 2a. Not only the 204 reflection is much more intense than the 20 -4, but the relative intensities of the other reflections are also significantly different for
positive and negative l values. Therefore the crystal structure cannot have hexagonal symmetry but is at most trigonal. The absence of any systematic absences observed on this and other zone axis diffraction patterns allows concluding that the unit cell must be primitive without any glide planes nor screw axes.

The Z-contrast image projected along the b-axis is displayed on figure 3a, with the corresponding projection of the 6H-B structure on figure 3b. The 7 bright spots observed in each segment of zig-zag lines correspond to alternating Ba and Ni or Sb columns (fig. 3b). The intensity profiles obtained from the boxed regions in figure 3a are displayed in figures 3c and 3d. The expected intensities (black lines) aren’t in agreement with the observed ones for the Ni and Sb columns. Instead of a clear difference in intensity due to the different atomic numbers, the intensities for both columns are very similar. A possible interpretation of this result is that throughout the thickness of the sample (between 10 to 50 nm) the columns contain roughly the same amount of Ni and Sb atoms.

Discussion

So how can these different observations be reconciled? The structure obtained from the XRPD and NPD refinements with the disorder between Ni and Sb do show a hexagonal unit cell with a 6\text{3} axis and a c glide plane. Electron diffraction shows that the symmetry of the crystal can be at most trigonal, without the 6\text{3} axis and the c glide plane. A threefold screw axis could also be excluded, which leads to several possible space groups, the highest symmetry of which is P3m1. In the 6H-B structure, the stacking order of the octahedra is \(-\text{A(Sb}^{5+})\text{-A(Sb}^{5+})\text{=}\text{A(M}^{2+})\text{-A(Sb}^{5+})\text{-A(Sb}^{5+})\text{-A(M}^{2+})\text{-A(Sb}^{5+})\text{-...}\), where A(C) denotes the octahedron layers occupied by cations C. The ”-“ sign represents corner sharing between layers and the “=“ sign represents face sharing. This stacking order is directly related to the presence of the 6\text{3} axis and c glide plane in the 6H-B structure. The lowering of the local symmetry to P3m1 (or lower) demonstrates that this stacking order can’t be maintained.

The stacking order of cation planes could then be \(-\text{A(Sb}^{5+})\text{-A(Sb}^{5+})\text{=}\text{A(M}^{2+})\text{-A(Sb}^{5+})\text{-A(M}^{2+})\text{-A(Sb}^{5+})\text{-A(Sb}^{5+})\text{-...}\) (fig. 4). In this case, the A(M\text{2+}) layers are separated alternately by one and three A(Sb\text{5+}) layers, while in the 6H-A and 6H-B stacking, the separation is always made of two such layers. Hence the disappearance of the 6\text{3} -axis and c-glide plane. If this stacking order occurs in domains of small dimensions (\(\approx\) 10 nm) but with inverted orders in neighboring domains, it is possible to obtain electron diffraction patterns from (mostly) one domain showing the correct symmetry, while XRPD and NPD show the average structure over many domains (fig. 4). Also, the Z-contrast images were probably obtained from a sample that
contained several domains in its thickness, the projection showing thus the average structure. More details can be found in Darie et al. [9].

**Conclusion**

In the investigation of a possible QSL material different diffraction methods gave apparently contradictory results: an ordered trigonal structure from electron diffraction and a disordered hexagonal structure from X-ray and neutron diffraction. This discrepancy is certainly important since the physical interpretation of the magnetic properties of the material depends on the correct local model. Therefore, it is important to remember the relevant length scales for these methods, electron diffraction being more local. Hence a model could be derived reconciling the local ordered structure with a global disordered structure.

**References**


Authors
Holger Klein$^1$, Céline Darie$^1$, Christophe Lepoittevin$^1$, Stéphanie Kodjikan$^1$, Pierre Bordet$^1$, Claire V. Colin$^1$, Oleg I. Lebedev$^2$

Affiliations
1 Institut Néel, Université Grenoble-Alpes and CNRS, Grenoble, France
2 Laboratoire CRISMAT, ENSICAEN, Caen, France

Contact
Dr. Holger Klein
Université Grenoble-Alpes and CNRS
Institut Néel
Grenoble, France