The impossible antiferroquadrupolar order of CeB_6

For three decades, the cubic rare-earth compound Cerium Hexaboride CeB_6 has been presented as the archetype of a type of ordering called "antiferroquadrupolar" (AFQ). The change in the lattice periodicity implies a symmetry lower than cubic for an AFQ state. Very accurate magnetic and magnetostriction measurements have now been done on CeB_6 at the Institut NEEL. They show that, in the supposedly antiferroquadrupolar phase, the crystal remains perfectly cubic...

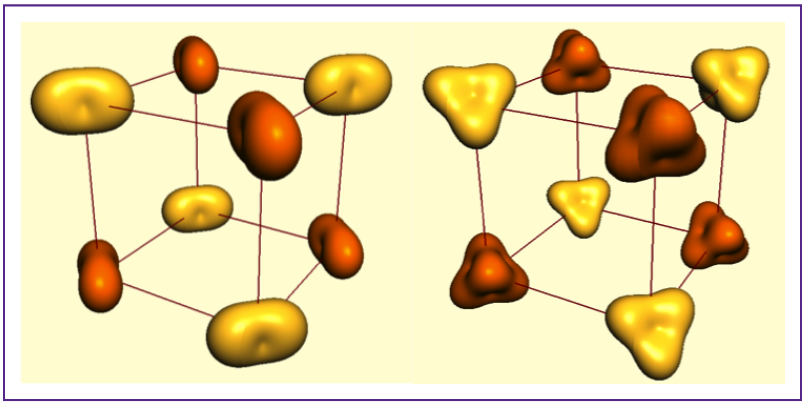

Fig.1: At left : example of an antiferroquadrupolar structure in CeB_6, as hitherto attributed to this compound, with [1/2 1/2 1/2] wave vector. The oblong shapes represent an aspherical angular distribution of the 4*f* electron of Ce^{3+}: the system is no longer cubic and the crystal must distort. At right : our proposed, octupolar structure with the same wave vector, that can be realised via a dynamical de-centering of the Ce^{3+} ions inside the boron cages. Perfectly cubic, this structure explains the absence of crystal distortions.

A quadrupolar order is of orbital nature : the atoms with unpaired electrons, in the 4f orbitals for the case of rare-earth atoms, collectively distort. This distortion of electronic charge clouds translates into the emergence of electric quadrupoles. In its antiferroquadrupolar variant, by analogy with antiferromagnetism, the distribution of the 4f electrons alternates from site to site.

In CeB_6, below a critical temperature "T_Q" = 3.3 K, macroscopic measurements (specific heat etc.) show that a new ordering develops. Neutron diffraction studies show that this order is not of magnetic nature. They also reveal an underlying difference between two kinds of Cerium sites that alternate on the cubic lattice according to the [1/2 1/2 1/2] wave vector. This has been interpreted as the consequence of an antiferroquadrupolar ordering. X-ray diffraction later confirmed that a charge distribution with *the* wave vector [1/2 1/2 1/2] develops below "T_Q".

Many subsequent experiments were systematically interpreted with a bias in favour of the antiferroquadrupolar scheme. However, there are obvious consequences of the antiferroquadrupolar hypothesis that have not been thoroughly investigated. Given the reported [1/2 1/2 1/2] wave vector, AFQ models for CeB_6 are necessarily of low symmetry (see Fig. 1, left side). Such a symmetry-lowering induced by quadrupoles is expected to result in large striction phenomena: in order to accommodate the new distribution of the 4*f* electron charge clouds, the crystal should anisotropically distort below "T_Q". Other properties of the system should reflect this anisotropy, in particular, the first-order magnetic susceptibility. Therefore, at the Institut NEEL, we undertook high accuracy measurements of the magnetic susceptibility and magnetostriction of CeB_6 below "T_Q", to check the symmetry properties of this supposed antiferroquadrupolar state.

As concerns the magnetic susceptibility, the result was surprising: Within the experimental accuracy, we found that the susceptibility is isotropic.

We then searched for distortions of the crystal using the Institut NEEL's high resolution magnetostriction apparatus, which can detect relative deformations as small as 10^{-7}. If there were a symmetry-lowering, the crystal would be expected to decompose into domains having different deformations. In which case, if the crystal is rotated in an applied magnetic field, its probed length should change abruptly as the field alternately selects different domains. No such effect could be detected. Studying as a function of temperature under magnetic field, we looked for tetragonal and trigonal distortion modes. Again, no specific effect could be observed while crossing the temperature T_Q.

This shows that the cubic symmetry of the crystal is preserved below the temperature "T_Q", which is strictly inconsistent with the antiferroquadrupolar interpretation. Furthermore, symmetry arguments show that, beyond quadrupoles, this cannot be accounted for by higher degree 4*f* electric multipoles.

In conclusion, alternative charge distributions have to be sought for, and one cannot ignore that rare-earth hexaborides realize a class of "cage-type" materials. Inside its cage of borons, a Cerium ion can dynamically move (vibrate) off-centre, thus realizing other kinds of charge distribution. At the right in Fig. 2, we propose an alternating octupolar distribution of the Cerium ion displacements that preserves the cubic symmetry of the crystal.

CONTACT
Mehdi AMARA
mehdi.amara@neel.cnrs.fr

FURTHER READING

CeB_6 macroscopically revisited
M. Amara and R.-M. Galéra
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