H6. COMPETING ORDER PARAMETERS IN LIGHT-RARE-EARTH HEXABORIDES

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Orbital phenomena associated with *d* electron states are known to be central to the physics of transition-metal oxides, and have been extensively studied. In the case of *f* electrons, which are subject to strong spin-orbit coupling, the proper description of orbital degrees of freedom is based on *multipoles*. Ordering phenomena involving higher-rank multipoles (quadrupoles, octu-poles, etc.) are currently attracting a great deal of interest, because they might account for several elusive phase transitions observed in rare-earth or actinide compounds ($Ce_{1-x}La_xB_6$, $SmRu_4P_{12}$, NpO_2, etc.). Multipole moments, being tensor quantities, can give rise to a variety of ordered states classified according to the symmetry of their order parameter. Interesting properties are expected to occur if a competition takes place between different types of order, involving multipole components of different symmetries. Such a situation may be realized in the cubic (CsCl-type) hexaboride compounds $Ce_{1-x}R_xB^6$ (*R*: Pr, Nd), where the light rare-earth Ce, Pr, and Nd have different mul-tiplet ground states (J = 5/2, 4, and 9/2, respectively), and thus different multipole moments.

CeB_6 is considered the archetype of a pure antiferro-quadrupolar (AFQ) order, realized in the so-called "phase II" below T_Q = 3.2 K, prior to the onset of a long-range magnetic order in "phase III" below T_N = 2.3 K [1]. In the latter phase, the Ce magnetic moments form a noncollinear, planar, 2*k*-*k*' structure, described by the 4 propagation vectors $\boldsymbol{k}_{1,2}$ = (1/4, ±1/4, 1/2) and $\boldsymbol{k}'_{1,2}$ = (1/4, ±1/4, 0). The preformed order of the O_{xy} (O_{yz}, O_{zx}) quadrupole moment components, with the wave vector $\boldsymbol{k}_Q$ = (1/2,1/2,1/2), produces a staggered anisotropy on the Ce sublattice, which is thought to be responsible for the unusual type of magnetic structure adopted by the system below T_N. Substitution of another rare earth ion (including La) strongly suppresses phase II, giving way to a rich pattern of ordered phases as a function of both concentration (Fig. 1) and applied magnetic field. Most of these phases have a clear magnetic signature, but quadrupole, and possibly higher multipole couplings are likely to play a role. The present study aims at understanding the microscopic mecha-nisms responsible for the stability of the different structures. Neutron diffraction measurements have been reported in Refs. [3,4] for $Ce_{1-x}Pr_xB_6$ and $Ce_{1-x}Nd_xB_6$, respectively. Here we present our results for the latter system, together with a brief discussion of their implica-tions as to a possible role of quadrupole interactions.

Powder and single-crystal experiments were performed on the multidetector diffractometer G4-1 and the lifting-counter diffractometer 6T2, using isotopic (^{11}B: 98.6%) samples prepared in Hiroshima.

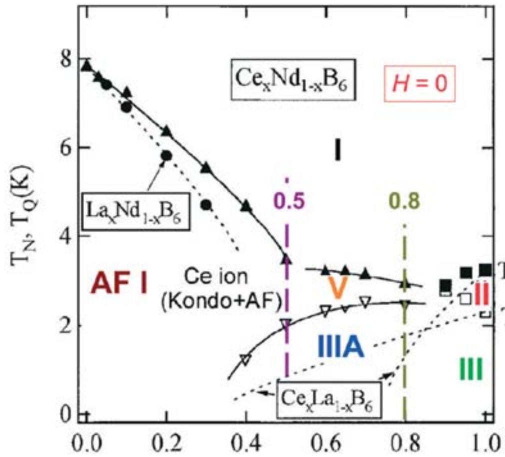

Figure 1. Phase diagram of $Ce_{1-x}Nd_xB_6$ in zero applied magnetic field; the vertical dashed lines cor-re-spond to the concentrations studied experimen-tally; $Ce_{1-x}La_xB_6$ data are plotted for comparison. (after Ref. [2])

The powder diffraction patterns (Fig. 2) reveal two clearly distinct regimes. For x = 0.5, the systems first orders below T_N in a simple AFI structure $\boldsymbol{k}_{AFI}$ = (0,0,1/2), similar to that found in pure NdB_6. Resistivity measurements suggest that, in this regime, the Ce ions are weakly coupled to the Nd magnetism and retain Kondo fluctuations inside the AFI ordered state. The fact that the 0 0 1/2 reflection is absent implies that the moment direction is parallel to the fourfold axis, pointing to an effect of ferroquadrupolar O^0_2 -type inter-actions between Nd moments as in pure NdB_6 [5]. For x = 0.8 (Fig. 2, upper frame), the structure forming below T_N is incommensurate with $\boldsymbol{k}_{inc}$ = (0.237, 0.237, 1/2). At lower temperature, a lock-in transition takes place to the commensurate (C) wave vector $\boldsymbol{k}_{com}$ = (1/4, 1/4, 1/2).

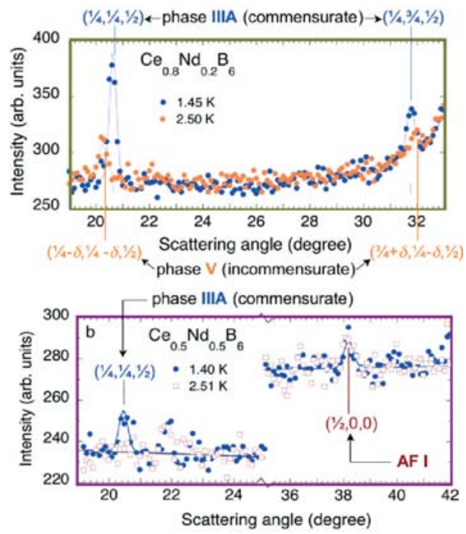

Figure 2. Powder diffraction patterns for $Ce_{1-x}Nd_xB_6$ (x = 0.8 and 0.5) mea-sured in the ground state at T_{min}⊕a 1.4 K and in the intermediate phase below T_N.

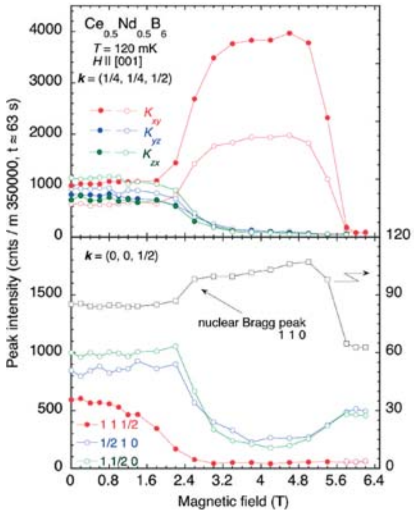

Figure 3. Field dependence of Bragg intensities for different C (upper frame) and AFI (lower frame) satellites at T = 120 mK.

This situation in phase IIIA is reminiscent of the compound PrB_6, where the structure was analyzed as 2-*k* and ascribed to an effect of quadrupole interac-tions between O_{xy}-type moments. The absence of ***k'***-type peaks, in contrast to the CeB_6 case, reflects the lack of long-range AFQ order associ-ated with $\boldsymbol{k}_Q$.

In the Nd-rich compound x = 0.5, the low-temperature transition again corresponds to the appearance of a commensurate component at $\boldsymbol{k}_{com}$ but, in this case, the high-temperature AFI reflections are not suppressed (Fig. 2, lower frame), suggesting that ordering behaviors associated with Ce and Nd moments somehow coexist.

This assumption is supported by the single-crystal results. At the lowest temperature of T = 120 mK, the intensity of the AFI peak 1 1/2 0 is indeed comparable to that of the C satellite 5/4 1/2 1/4. When an external field is applied along [001], the intensities plotted in Fig. 3 indicate a repopulation of the C domains above $H_1 \oplus 2.4$ T (upper frame), consistent with the hypothesized 2-*k* planar, PrB_6-like structure. More surprisingly, this change is accompanied by a steep suppression of the Bragg peaks associated with the AFI single-*k* domains k_x and k_y (lower frame). Those associated with k_z, on the contrary, decrease smoothly to zero from H = 0 to 2.4 T. This leads us to propose that the AFI (k_x and k_y) and C (k^c_{y2} and k^c_{2x}) components are actually coupled by pairs (e.g. k^c_{y2} with k^c_x), and contribute to one and the same structure within a given domain. We further speculate that the two components may reflect, respectively, the Ce and Nd contributions, with Ce moments forming a structure similar to the planar 2-*k* state mentioned above, and Nd moments an approximately AFI state along the normal to the planes. In this picture, the

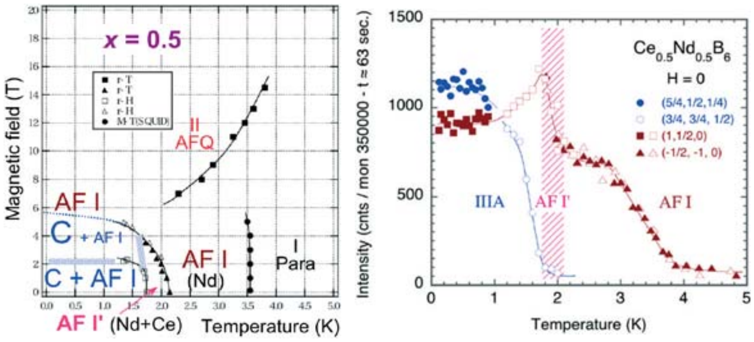

Figure. 4. (*left*): (H,T) magnetic phase diagram of $Ce_{0.5}Nd_{0.5}B_6$ (data for bulk measurements from Kawaguchi et al.). (*right*): T dependences of the intensities of C and AFI satellites at H = 0.

effect in low fields implies no true domain repopulation but a mere reorien-tation of the Nd moments within the k^c_{xy}- k_z domain.

Above a second transition field H_2 = 5.4 T, the C structure is steeply suppressed, and AFI order is restored, with only the two domains k_y and k_z populated. This is consistent with moments oriented, within each domain, along the propagation vector. In high fields, no evidence was found for the AFQ transition line derived from bulk measurements. The results in applied fields are summarized by the phase diagram drawn in Fig. 4.

Finally, we want to point out the interesting observation of an intermediate region in the phase diagram, between 1.7 and 2.5 K in zero field, which is characterized by a steep increase in the AFI component just before the C order sets in. We believe that it denotes the ordering of Ce moments in the existing AFI structure of Nd, likely associated with the suppression of Kondo fluctuations.

In conclusion, the complex pattern of ordered phases found in the $Ce_{1-x}Nd_xB_6$ solid solutions appears to reflect the rather unique competition of two different types of quadrupolar couplings, predominantly FQ between the Nd O^0_2 moments, and AFQ between the Ce O_{xy}-type moments. Neutron diffraction under conditions of high magnetic fields and very low temperatures has proved invaluable in revealing the details of the magnetic phases. It should now be complemented by x-ray synchrotron measurements to probe directly the order of multipole moments.

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