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MAGNETIC STRUCTURES DETERMINED BY NEUTRON DIFFRACTION IN THE $EuB_{6-x}C_x$ SYSTEM

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Magnetic structures of pure and carbon-doped europium hexaboride $EuB_{6-x}C_x$, were determined by neutron diffraction on powders prepared from ^{11}B and ^{153}Eu. EuB_6 is a simple ferromagnet, whereas the x = 0.20 compound has an incommensurate spiral structure with propagation vector τ = (0.28, 0, 0). Data for a magnetically inhomogeneous intermediate composition, x = 0.05, indicate a mixture of ferromagnetic and helimagnetic domains with τ = (0, 0, 0.104). Helimagnetism in $EuB_{6-x}C_x$ arises from a competition between ferromagnetic near-neighbour exchange and antiferromagnetic interactions due to conduction electrons.

The relation between the magnetic properties and the electronic structure of europium hexaboride EuB_6 has been the subject of many experimental and theoretical studies[1-10]. It was difficult to decide whether the compound is intrinsically a semiconductor or a semimetal, because of the small gap (≃ 0.1 eV). Furthermore the role of the impurities and possible cation vacancies could not be neglected[1]. Nevertheless a recent work suggests that EuB_6 is a narrow-gap intrinsic semiconductor in the paramagnetic state, and becomes a semimetal or a metal when it orders magnetically[7, 9].

Semiconducting behaviour arises for $M^{2+}B_6$ hexaborides because the bonding bands of the boron network are filled up by transfer of two electrons from the cation[11, 12].

EuB_6 can be doped either by substitution of a tri- or tetravalent cation or by replacing some boron atoms by carbon[2, 4, 6, 13, 14]. In both cases, substitution yields n-type metallic conductors[6]. The conduction electrons modify the magnetic interactions and induce a sign change of the paramagnetic Curie temperature θ_p.

Data shown in Fig. 1 concern the ternary compound $EuB_{6-x}C_x$. The lattice parameter decreases from 4.1855 Å for x = 0 to 4.1685 Å for x = 0.21, the limit of the single phase range. θ_p changes sign at x ≃ 0.13, but the magnetic ordering temperature passes through a minimum around x = 0.06. The ordering temperature was defined by appearance either of magnetic hyperfine splitting in the ^{151}Eu Mössbauer spectrum[4] or of a peak in the magnetization measured in a constant small field[3]. This cusp disappears in fields of 1.2 - 3 kOe when x ≃ 0.10, but persists in fields greater than 10 kOe for x = 0.21.

Our Mössbauer study revealed a temperature-dependent broadening of magnetic hyperfine lines for x = 0.05 (absent for x = 0 and x = 0.21), which implies that the exchange interactions are inhomogeneous on a microscopic scale[4]. This result together with magnetization curves at 4.2 K, which show that 90 % of the saturation is achieved in fields of less than 5 kOe for EuB_6, but that 100 kOe is required to produce the same degree of saturation in the x = 0.21 sample[3], suggest strongly that the magnetic order evolved from ferromagnetism (x = 0) to antiferromagnetism (x = 0.21), via an intermediate mictomagnetic phase.

To test these hypotheses, a series of neutron diffraction measurements has been undertaken on samples with x = 0, 0.05 and 0.20. Powder samples of $EuB_{6-x}C_x$ were prepared by reduction of Eu_2O_3 (99.999 %) with boron or boron-carbon mixtures[2]. Since natural boron and europium are both intense absorbers of thermal neutrons, all three samples were made from boron enriched to 99.3 % in ^{11}B. Furthermore we also used a single euro-

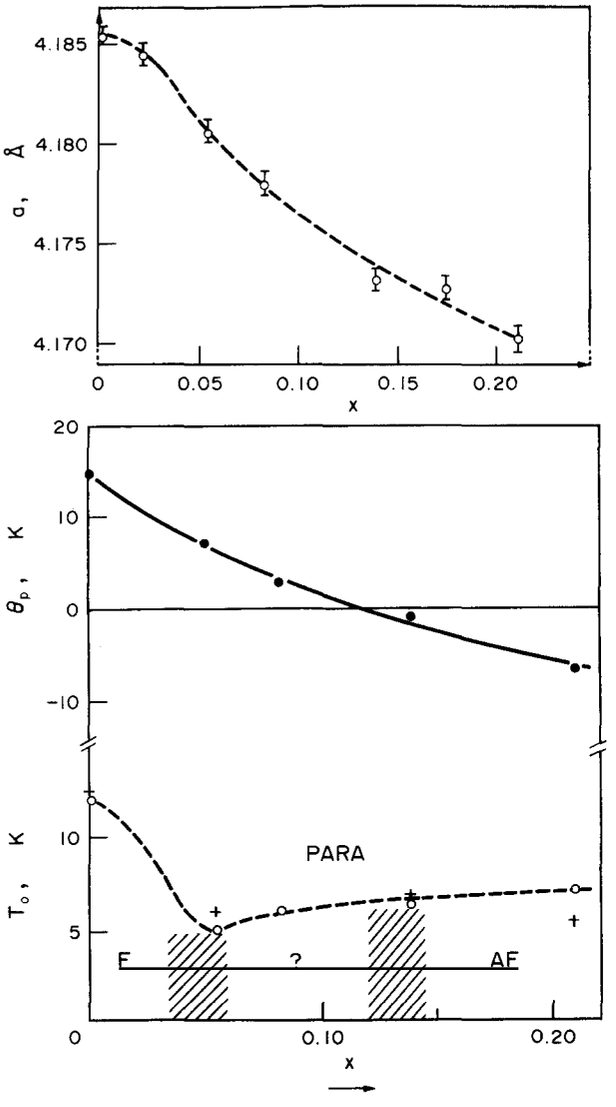

Fig. 1 Data for carbon substituted europium hexaboride $EuB_{6-x}C_x$ (a) lattice parameter at 300 K. (b) Paramagnetic Curie temperature obtained by extrapolation. (c) magnetic ordering temperature derived from Mössbauer (black circles) and susceptibility measurements (crosses).

pium isotope, ^{153}Eu, for the x = 0.05 sample.

Neutron measurements have been performed on the powder goniometer DIB at the ILL, GRENOBLE, which is equipped with a linear multidetector allowing simultaneous recording of 400 points in the range $2° < \theta < 42°$.

The neutron wave-length was 2.52 Å. 300-500 mg powder samples were placed in the 1 mm gap between the cylindrical double wall of a vanadium sample holder tube. Transmission was 5 % for $Eu^{11}B_6$ and $Eu^{11}B_{5.8}C_{0.2}$ and 92 % for $^{153}Eu^{11}B_{5.95}C_{0.05}$. The intensities of the nuclear and magnetic reflections have all been corrected for sample absorption[15].

EuB_6

Neutron diffraction diagrams have been recorded above and below the magnetic ordering transition ($T_C \simeq 12.5$ K). At 17 K, only nuclear reflections are observed. Refinement of the crystal structure was made on the four reflections (001), (011), (111) and (200) in the space group, Pm3m with europium in (1a) position 0, 0, 0 and boron in (6f) position u, 1/2, 1/2. The scattering lenghts used were 0.68×10^{-12} cm for natural europium and 0.67×10^{-12} cm for ^{11}B.

Results of the refinement given in Table I are in good agreement with values determined by X-ray diffraction.

Below T_C, at 3 K, no supplementary lines appear, but the intensities of the four nuclear reflections condidered above increase considerably. The difference between the scattering at 3 K and 17 K, shown in Fig. 2, characterizes a ferromagnetic structure having the same periodicity as the nuclear cell. The data lead to a magnetic moment on europium of $7.3 \pm 0.5\ \mu_B$ (the error comes mainly from uncertainty in the absorption). The orientation of the magnetic moment is undetermined.

TABLE I

Crystallographic data for EuB_6 and $EuB_{6-x}C_x$

Compounds	Parameter a (Å)	T(K)	u boron position	Thermal parameter B	Residual R %
EuB_6	4.19 (1)	17	0.2043(5)	0.65(5)	3.8
$^{153}Eu^{11}B_{5.95}C_{0.05}$	4.17 (1)	10	0.2043(9)	0.50(5)	3.8
$Eu^{11}B_{5.8}C_{0.2}$	4.16 (1)	7	0.2043(5)	0.50(5)	3.2

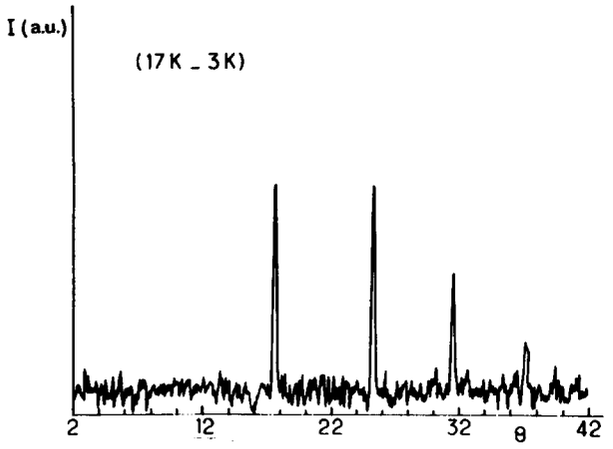

Fig. 2 Difference between neutron scattering intensities from a $Eu^{11}B_6$ sample powder at 3 and 17 K (T_C = 12.5 K).

$^{153}EuB_{5.95}C_{0.05}$

This borocarbide has its magnetic transition at 5.2 K, so neutron diffraction diagrams have been recorded at 10 K and 1.7 K. They are shown in Fig. 3 together with their intensity difference. The refinement of the crystal structure was carried out from the 10 K spectrum supposing boron and carbon atoms to be randomly distributed (Table I). This refinement also gave the ^{153}Eu nuclear scattering-length, 0.845 ± 0.008 10^{-12} cm.

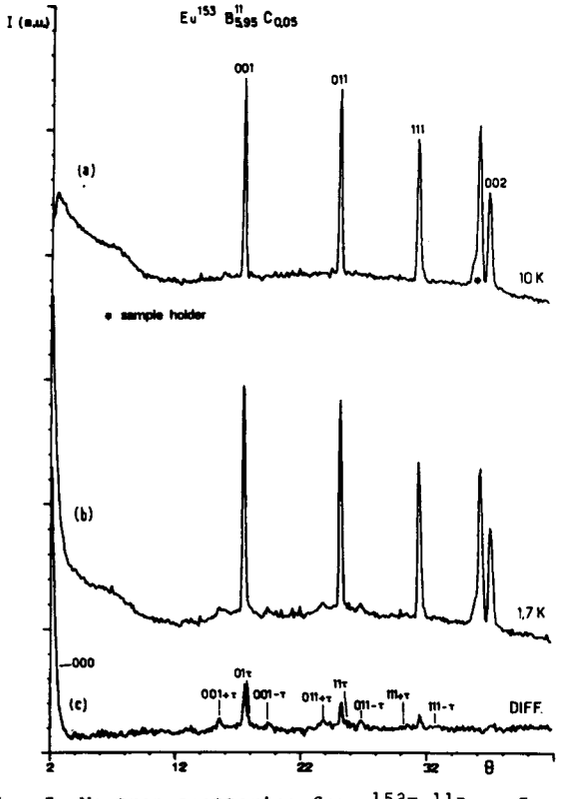

Fig. 3 Neutron scattering from $^{153}Eu^{11}B_{5.95}C_{0.05}$ sample powder (a) at 10 K (b) at 1.7 K and (c) the difference diagram. The magnetic ordering temperature is 5.2 K.

The diagram recorded at 1.7 K shows that the nuclear reflections are accompanied by magnetic satellite lines and that there is broad additional scattering under each nuclear peak. Furthermore, the difference diagram reveals the presence of magnetic lines in the same positions as the nuclear peaks. The magnetic satellites have been indexed using a propagation vector $\tau = [0, 0, 0.104]$, incommensurate with the crystal lattice. As for EuB_6, the direction of τ is undetermined.

The refinement of the magnetic structure has been made separately on two types of reflections, magnetic satellite peaks and magnetic peaks coinciding with nuclear reflections. The magnetic moments are respectively $\mu_1 = 5 \pm 0.5\ \mu_B$ and $\mu_2 = 3.6 \pm 0.2\ \mu_B$. The magnetic structure can therefore be described either as a ferromagnetic (conical) spiral with a magnetic moment of $6.2 \pm 0.6\ \mu_B$ making an angle of 54° with the direction of the propagation vector or as a mixture of two magnetic domains, respectively ferromagnetic and helimagnetic.

$EuB_{5.8}C_{0.2}$

Neutron diffraction diagrams have been determined at 22 K and 1.7 K above and below the magnetic ordering temperature (5.6 K). The refinement carried out from the nuclear reflections in the paramagnetic temperature range again confirms the cubic crystal structure (Table I). In contrast to previous $^{153}Eu^{11}B_{5.95}C_{0.05}$, no magnetic contribution to the nuclear reflections was found at 1.7 K. The magnetic peaks can be indexed with a propagation vector $\tau = [0, 0, 0.28]$, the magnetic structure can be described as a simple helimagnetic spiral incommensurate with the lattice. Supposing τ to be in the $\vec{c}$ direction, the magnetic moment in the $\vec{a}$ $\vec{b}$ plane is of magnitude $6 \pm 0.5\ \mu_B$. The value of the magnetic moment is less than expected. Due to high absorption it was not possible to detect any broad peak in the diffuse background. In three diagrams recorded at different temperatures below 5.6 K there was no indication that the propagation vector depends on temperature.

The magnetic structures of EuB_6, and $Eu^{11}B_{5.8}C_{0.2}$ are represented in Fig. 4. Our measurements show at 3 K no sign of anything but ferromagnetism in pure EuB_6 well below the Curie point, but in view of unusual magnetic specific heat (5) it is worth stating what deviations from simple ferromagnet ordering

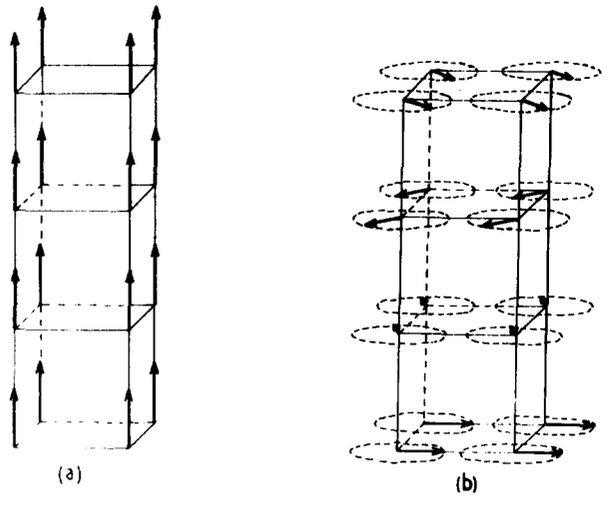

Fig. 4 Schematic representation of magnetic structures of (a) ferromagnetic EuB_6 (b) helimagnetic $EuB_{5.8}C_{0.2}$. The direction of the propagation vectors are arbitrary chosen to be along [001] direction.

could be consistent with this result. A helix with a period greater than about 100 a would be effectively indistinguishable from a ferromagnet. Furthermore a mixed structure like that of $EuB_{5.95}C_{0.05}$ with a helimagnetic component of magnitude 1 μ_B or less gives rise to satellites which would be completely lost in the background noise.

An increase of ferromagnetic exchange interactions with rising temperature could account for the exceptionnaly flattened temperature dependence of the magnetization and hyperfine field, and the broad specific heat anomaly. This may be due to the fall in conduction electron concentration in ferromagnetic EuB_6 as the temperature approaches T_C[7, 10]. From the behaviour of $EuB_{6-x}C_x$ we see that conduction electrons produce antiferromagnetic interactions, so that the net ferromagnetic interaction in EuB_6 will increase as $T \to T_C$.

At the other extreme, the magnetic structure of $EuB_{5.8}C_{0.2}$ has been found within experimental accuracy to be a simple spiral. Helimagnetic structures will then arise from competing exchange interactions with different shells of neighbours. In particular, the interactions, with neighbours at 2a must be antiferromagnetic for a spiral ground state.

The sample with an intermediate carbon content (x = 0.05) shows a magnetic structure itself intermediate between the two extremes of ferromagnetism at x = 0 and helimagnetism at x = 0.20. The neutron data could be interpreted either in terms of a mixture of ferromagnetic and helimagnetic domains or in terms of a single phase with a conical spiral structure.

Although there is no sign of any two phase-mixture in the X-ray diffraction patterns, nevertheless we favour the former interpretation, as the available anisotropy is not strong enough for Eu^{2+} ($^8S_{7/2}$) in a simple cubic lattice to stabilize a conical spiral structure. There is also a substantial amount of scattering in the broad region at the base of the peaks which could be associated with small incoherent regions, magnetically ordered, whose size would be about 50 Å. These regions could be associated with local fluctuations in the carbon concentration, producing carbon-richer helimagnetic domains and carbon-poorer ones where the balance of exchange interactions with neighbouring Eu atoms is below the threshold required by appearance of helimagnetism. The ferromagnetic domains are not coherent in the x = 0.05 sample, but their moments are distributed at random in directions determined by the exchange with their surroundings. This picture is consistent with the neutron data and the observed behaviour of susceptibility and magnetization[3], as well as with the Mössbauer data[4] which led originally to the suggestion of mictomagnetism in this concentration range.

We may notice that the magnetic satellite lines are well separated from the central line for the x = 0.05 sample. This can result from a weak anisotropy which rules out any helimagnetic structural with a very long period.

In summary, as the conduction electron concentration is raised, magnetic ordering in EuB_6 goes from ferromagnetic through a series of incommensurate helimagnetic structures of decreasing period.

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