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Cr_3 Triangles induced competing magnetic interactions in the new metal boride $TiCrIr_2B_2$: An NMR and DFT study

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ABSTRACT

The presence of one-dimensional trigonal arrangements of chromium atoms (Cr_3) in the structure of $TiCrIr_2B_2$ leads to a magnetic transition near ambient temperature. Herein we report an investigation of the nature of electronic and magnetic properties of $TiCrIr_2B_2$ via *ab initio* calculations together with ^{11}B NMR Knight shift (K) and spin-lattice relaxation rate ($1/T_1$) analysis. The presence of a characteristic rectangular powder pattern below 280 K, absence of a Korringa relation, strong enhancement of $1/T_1.T$ at low temperatures and weak temperature dependence of K indicate competition between antiferromagnetic and ferromagnetic spin fluctuations in the itinerant *d*-band electrons, in agreement with *ab initio* calculations. One-dimensional trigonal arrangements of magnetically active elements in intermetallic compounds, as is found in $TiCrIr_2B_2$, are quite rare and could lead to exotic phenomena such as spin-chirality and quantum criticality in low-dimensional frustrated lattices.

1. Introduction

Geometrically frustrated magnetism occurs when three spins are arranged in a triangle and interact antiferromagnetically with their neighbors. In this case it is impossible for all three spins to be aligned antiparallel to their neighbors at the same time. The system is said to be frustrated. Triangular arrangements of magnetic elements are of high interest because they may lead to exotic ground states such as spin glasses, chiral spin liquid and quantum criticality [1,2]. Most research in this area is focused on two or three-dimensional trigonal arrangements such as pyrochlores, kagome and triangular lattices. Examples of one-dimensional trigonal arrangements in intermetallic compounds, as was found in $TiCrIr_2B_2$, are quite rare [3]. Other examples include the compounds CrNbX (X = Si, Ge) (ZrNiAl-type structure) [4]. Here, the chromium atoms also form one-dimensional structures. We performed measurements of the ^{11}B NMR Knight shift (K) and nuclear spin-lattice relaxation rate ($1/T_1$) in $TiCrIr_2B_2$ at temperatures ranging from 150 to 420 K. Near the magnetic transition temperature, around 280 K, the ^{11}B resonance exhibits the typical rectangular powder pattern [5], accompanied by a negative temperature-dependent Knight shift, indicating the presence of a dominant *p-d* hybridization state of the hyperfine interaction in the vicinity of the boron environment rather than the *s*-contact term. Our results are interpreted as resulting from spin fluctuations driven by competing ferromagnetic and antiferromagnetic interactions. The absence of Korringa relation and a strong upturn in $\frac{1}{T_1 . T}$ at low temperatures support the presence of low-energy magnetic fluctuations and the itinerant *d*-band character of $TiCrIr_2B_2$.

2. Materials and methods

Samples of $TiCrIr_2B_2$ were synthesized by arc-melting the elements in a water-cooled copper crucible under argon atmosphere. A tungsten tip was used as second electrode. Only high purity elements were used (at least 99.9%). With a starting ratio of Ti:Cr:Ir:B = 1:1:2:2 (0.5 g total), the elements were pressed into pellets and melted several times under argon atmosphere (purified over silica gel, molecular sieve and Ti sponge at 950 K) until homogeneous melting was achieved. A sphere of metallic lustering surface and stable in air was obtained. To obtain enough material for solid-state nuclear magnetic resonance (NMR) measurements, three samples were synthesized and ground together. The purity of the samples was checked by X-ray powder diffraction (PXRD) on a STOE STADI P diffractometer using Cu-K(α1) radiation.

For phase analysis, a Rietveld refinement of room temperature PXRD data was performed. The refinement was carried out using the

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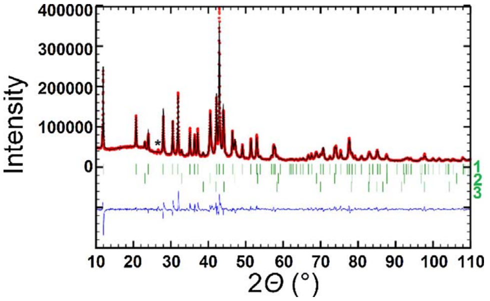

Fig. 1. Rietveld refinement of a powder XRD pattern of $TiCrIr_2B_2$. *: SiO_2 peak. Bragg positions of (1) $TiCrIr_2B_2$, (2) $TiIr_3$ and (3) CrIr are shown in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

FULLPROF software [6]. The structure of a single crystal of $TiCrIr_2B_2$ was used as a model.

The magnetic measurements were performed on polycrystalline samples with a SQUID magnetometer (MPMS, Quantum Design, San Diego, USA) across the temperature range 2–400 K and at external fields of 0.01 and 0.1 T. High-temperature measurements (400–600 K) were performed on a Physical Properties Measurement System (PPMS, Quantum Design, San Diego, USA) at different magnetic fields. The magnetic transition temperature was determined by linearly fitting the steepest part of the magnetization curve in a field of 0.01 T. The intersection of the fit with the x-axis yields the critical temperature (T_c).

The NMR experiments were carried out on a Bruker DSX-300 spectrometer. The chemical shift was confirmed and calibrated with the ^{11}B resonance of an aqueous solution of boric acid (pH = 4.4) [7–9] by using the Ξ scale [10,11].

3. Results and discussion

A Rietveld refinement of the PXRD pattern is shown in Fig. 1 with $TiCrIr_2B_2$ as the main phase [weight percentage, 78(5)%]. $TiIr_3$ could be indexed as a second phase [19(2)%], and its lattice parameters are enlarged compared to those published in the literature [12]. The enlargement indicates boron incorporation (expected at the temperature of synthesis) into the Ir_6-octahedra in $TiIr_3$ leading to $TiIr_3B_x$. Additional small reflections were found and could be indexed as non-stoichiometric Cr_xIr_{1-x} alloy (space group: *P6₃/mmc*) [13]. The amount of Cr_xIr_{1-x} is 3(1)% [3]. The lattice parameters obtained for $TiCrIr_2B_2$, a = 8.560(4) Å and c = 3.189(2) Å, are in excellent agreement with those found from earlier single crystal analysis [3]. In comparison with the lattice parameters of the parent phase $Ti_{1.6}Os_{1.4}RuB_2$ [a = 8.554(14) Å; c = 3.0336(7) Å] the a parameter is very similar, while the c parameter is significantly larger in $TiCrIr_2B_2$. $TiCrIr_2B_2$ crystallizes in the hexagonal $Ti_{1+x}Os_{2-x}RuB_2$ structure type (*space group* $P\bar{6}2m$, *No. 189*). The $Ti_{1+x}Os_{2-x}RuB_2$ structure type was first published in 2006 and gained interest because it was the first structure that contained trigonal planar B_4-units [4]. In Fig. 2(a) the unit cell of $TiCrIr_2B_2$ is depicted. It consists of two different layers along the c-axis (Fig. 2b bottom). One layer at z = ½, contains B_4-fragments as well as Ir-atoms. The other layer at z = 0 contains isolated boron atoms as well as chromium and titanium sites.

Single crystal X-ray diffraction (SCXRD) refinements showed no mixed occupancies for all metal sites [3], as was found in the parent compound $Ti_{1+x}Os_{2-x}RuB_2$. These results were also supported by density functional calculations (DFT), which confirmed the presence of site preference for the 3*d* metals Ti and Cr in their respective sites [3]. A detailed description of the crystal structure and analysis is given in [3]; we will only focus on the boron surroundings which are relevant to the understanding of the NMR data. B1 and B2 atoms are arranged in a trigonal planar B_4-unit as shown in Fig. 2 (top). The B-B distance within the unit is 1.76 Å. The B1 atom lies in a trigonal prism of chromium atoms (Cr_6B), capped on its quadrangular faces by boron atoms (B2). The Cr_6B prisms are stacked on each other, forming chains along the c-axis. The intra triangle Cr-Cr-distance is 2.64 Å, while the distance between two triangles is 3.18 Å. The chains are geometrically isolated from each other with a chain-chain distance of 8.55 Å. The B_3 atom is found in the z = 0 layer, coordinated by a trigonal prism of iridium atoms (Fig. 2c, bottom).

Magnetic measurements performed over the temperature range 2–600 K and at an external magnetic field of 0.1 T indicate a ferrimagnetic behavior with a critical temperature around 275 K and a Weiss constant Θ of −755 K, indicating the presence of strong antiferromagnetic interactions [3]. DFT calculations have proposed a canted, nonlinear magnetic ground state ordering in the new phase [3]. Fig. 3 shows the Cr- and B-partial non-spin polarized (bottom) and spin polarized (top) density of states (DOS) of $TiCrIr_2B_2$, indicating that the main contributor to the magnetic ordering is Cr but also that the contribution from boron cannot be ignored. Similar examples [14–16] have been reported in other systems where the boron atoms mediate and indirectly (through the site preference and bond length) contribute to magnetic interactions. In fact, the non-spin-polarized results show that E_F falls on a peak of the DOS for both Cr and B, a sign of electronic instability. Upon spin-polarization, majority and minority spins of Cr *d*-states split, leading to a pseudogap at E_F. Boron E_F DOS are mainly contributed by B *p*-states, majority and minority spins of which also slightly split upon spin-polarization. This indicates a strong mixture of B *p*-states and Cr *d*-states in $TiCrIr_2B_2$, a result supported by the NMR findings below.

The observed critical temperature and negative Weiss constant indicate a mixture of ferromagnetic and antiferromagnetic interactions. A hysteresis was also reported at 5 K with a field ranging from −5 to +5 T [3]. The magnetization does not reach saturation at ± 5 T, where its magnetic moment is only 0.05 μ_B. The hysteresis curve shows a coercivity of 12 kA/m and lies in a regime of semi hard magnets. At low temperatures (below 50 K) the magnetic moment begins to increase

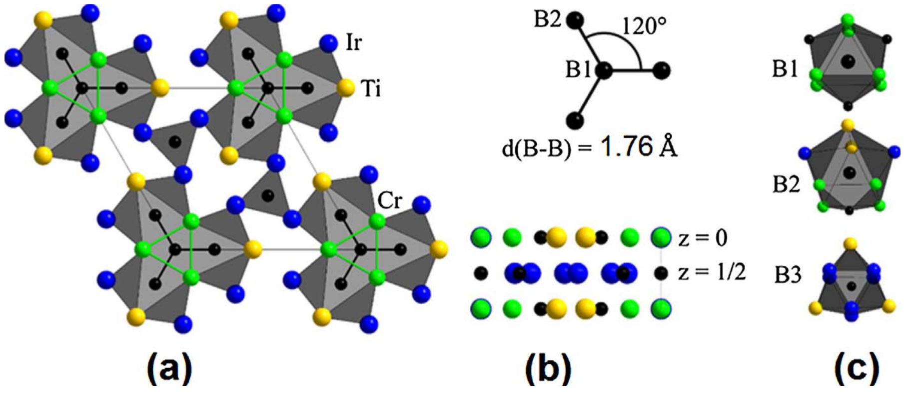

Fig. 2. Crystal structure of $TiCrIr_2B_2$ (green: Chromium; blue: Iridium; yellow: Titanium; black: Boron) (a) unit cell of $TiCrIr_2B_2$ along the c-axis. (b) B_4-unit and unit cell along a-axis showing the layer-like structural arrangement. (c) Coordination polyhedra of boron sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).