Antiferromagnetic metal BaCr$_2$As$_2$ – is there a chance for superconductivity?


While in doped variants of BaFe$_2$As$_2$ superconductivity with $T_c$ up to 55 K had been observed, until now no trace of this phenomenon has been seen in corresponding isostructural materials with Mn or Cr. In a collaborative effort, the structural, electronic and magnetic properties of the chromium analogue BaCr$_2$As$_2$ were investigated. BaCr$_2$As$_2$ is an antiferromagnetic metal with high Néel temperature of 580 K but rather low ordered magnetic moment of 1.9 $\mu_B$. Under high pressure a collapse of the tetragonal structure is observed, however no superconductivity is induced. A study of the band structure with ARPES reveals that electronic correlations are weaker in BaCr$_2$As$_2$ (3$d^4$ configuration) than in the 3$d^5$ (Mn) counterparts and the iron superconductors.

Introduction

It was a great surprise in 2008 when superconductivity (sc) with a quite high $T_c$ of 26 K was discovered in an iron-arsecenic compound [1]. Compounds containing iron – the prototype element for strong ferromagnetism and therefore antagonist to sc – were long thought to be no candidates in the search for sc. Fe-based sc’s (FeSCs) crystallize in “1111,” “122,” “111,” and “11” type structures built up from edge-sharing FeAs or FeSe tetrahedra [2]. Starting from the “122” type mother compound BaFe$_2$As$_2$, sc can be induced by doping either holes (e.g. by substitution of Ba with K) or by substitution of the Fe by Co, Ni, etc. (electron doping), or even by isovalent substitutions of Ru for Fe or P for As [2]. Remarkably, no sc has been found yet for substitutions with Mn or Cr, i.e. elements with lower 3$d$ electron count than Fe [3]. As in many unconventional sc’s, in the phase diagram of the FeSC compounds the sc phase lies in the proximity of a magnetically ordered phase. Thus, electron correlation effects seem to be important, with the Hund’s exchange interaction being the major effect in FeSCs. Such correlations should be strongest for materials where the 3$d$ electron shell is half filled (Mn and hole-doped Fe compounds) and decrease towards higher and lower 3$d$ electron counts. Consequently, there have been suggestions [4,5] that sc may occur in suitably modified Cr pnictides. Indeed, the recent discovery [6] that CrAs under mild pressure (0.8 GPa) becomes nonmagnetic and finally sc has spurred efforts to search for sc in other Cr-based compounds.

Antiferromagnetism of BaCr$_2$As$_2$ and BaCrFeAs$_2$

In the literature, from DFT-based electronic structure calculations it had been suggested that the Cr analogue to BaFe$_2$As$_2$ is a G-type antiferromagnet, with the physical properties being in accordance with

![Fig. 1: Temperature dependence of the magnetic moments per transition-metal atom in BaCr$_2$As$_2$ and BaCrFeAs$_2$ as obtained from powder neutron diffraction data (instruments E2, E6, and E9 at BER II).](image)

this conclusion [7]. To prove that ground state, we have prepared high-quality single crystals of the compound by the Bridgman method. Investigations of the anisotropic magnetic susceptibility, the specific heat, and by powder neutron diffraction consistently show a $G$-type antiferromagnetic (afm) order for below $T_N = 580$ K (Fig. 1 [8]). The ordered moment $\mu_G = 1.9 \mu_B$ is low. Very similar values of $T_N$ and $\mu_G$ have recently been reported for isostructural SrCr$_2$As$_2$ and EuCr$_2$As$_2$ [9,10]. All these compounds are metallic, in contrast to the corresponding Mn compounds MMn$_2$As$_2$, which are Mott insulators, as predicted by theory [11]. We also prepared single crystals of BaCrFeAs$_2$. This compound with a nominal d electron count of 5 is a bad metallic conductor with an afm ordering at $T_N = 265$ K and $\mu_{Cr/Fe} = 1.1 \mu_B$ only, in contrast to its Mn analogue. By $^{57}$Fe Mössbauer spectroscopy we could prove that the Fe species actually contribute only a small ordered moment $\mu_d$ to the G

- type order is unfavorable for Fe [8]. The question arises whether it is possible to achieve sc starting from these afm Cr compounds?
High-pressure study of BaCr$_2$As$_2$ [13]

In a number of Fe-pnictides $x$ may be induced or the $T_c$ may be dramatically enhanced by the application of high pressure [12]. Therefore, we have investigated the crystal structure as well as the electrical transport of single-crystalline BaCr$_2$As$_2$ at pressures up to 35 GPa. At a pressure of about 18.5 GPa an isostructural phase transition to a collapsed tetragonal phase is observed (Fig. 2, left), similar to that in BaFe$_2$As$_2$. In both phases, BaCr$_2$As$_2$ is a normal metal. Electronic structure calculations suggest the metallic and $a^*$f ground state with $G$-type magnetic order to persist for the collapsed tetragonal phase. From DFT calculation, the collapse of the magnetic moment of Cr is predicted at about 80 GPa (Fig. 2 right). The stable Néel-type $a^*$f in BaCr$_2$As$_2$ and the corresponding Mn compound is in strong contrast to the stripe-type magnetic order typical for BaFe$_2$As$_2$ and related compounds and which is easily suppressed, e.g., by a suitable chemical doping.

![Fig. 2: Left: synchrotron x-ray diffraction patterns of BaCr$_2$As$_2$ under high pressure. The peaks are indexed in space group I4/mmm. Right: pressure dependence of the calculated spin magnetic moment.](image)

Correlation effects in BaCr$_2$As$_2$ – an ARPES study [14]

The electronic structure and especially the strength of electronic correlation in BaCr$_2$As$_2$ was studied by angle-resolved photoemission spectroscopy (ARPES) and first-principles calculations. The experimental ARPES (Fig. 3) is in good agreement with the calculated band structure. A comparison of the experimental and calculated effective masses yields a correlation-induced mass renormalization $m^*$ close to unity for BaCr$_2$As$_2$. This is in contrast to FeSCs, where it ranges between 2 and 4. In addition, the lifetime broadening of the experimentally observed dispersions further corroborates our conclusion that correlations are much weaker in BaCr$_2$As$_2$ ($d^0$) than in Fe-based materials and other systems with a $3d$ electron count closer to five. This is supported also by the finding that, in contrast to Fe-pnictides, where due to correlation effects the $3d_{xy}$ pocket is shifted above the Fe $3d_{x^2-y^2}$ hole pockets, in BaCr$_2$As$_2$ the $3d_{xy}$ pocket remains below the $3d_{x^2-y^2}$ pockets. The present study on the Cr compound showing a reduced scattering rate and a negligible band renormalization, compared with hole-doped Fe-pnictides, confirms the theoretical predictions that Hund’s exchange interaction is most important in these materials.

![Fig. 3: ARPES intensity (left) and energy-momentum distribution map (right) along $S'$-$F$-$S'$ parallel to $k_z$ using $s$ polarized photons with energy of 70 eV of BaCr$_2$As$_2$. The spectra were taken with synchrotron radiation at the BESSY II facility, Berlin.](image)

References


* Walter.Schnelle@cpfs.mpg.de

1 Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin
2 MPI of Microstructure Physics, Halle (Saale)
3 Rutgers University, Piscataway, NJ, USA
4 Shubnikov Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia
5 University of West Bohemia, Pilsen, Czech Republic
6 Leibniz Institute for Solid State and Materials Research, Dresden
7 Dresden University of Technology, Dresden