

Antiferromagnetic metal BaCr_2As_2 – is there a chance for superconductivity?

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While in doped variants of BaFe_2As_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_2As_2 were investigated. BaCr_2As_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_2As_2 ($3d^4$ configuration) than in the $3d^5$ (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-arsenic 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_2As_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 $3d$ 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 $3d$ electron shell is half filled (Mn and hole-doped Fe compounds) and decrease towards higher and lower $3d$ 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_2As_2 and BaCrFeAs_2

In the literature, from DFT-based electronic structure calculations it had been suggested that the Cr analogue to BaFe_2As_2 is a G -type antiferromagnet, with the physical properties being in accordance with

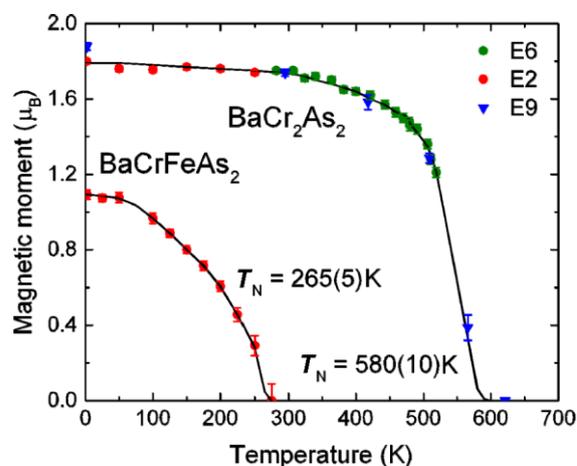


Fig. 1: Temperature dependence of the magnetic moments per transition-metal atom in BaCr_2As_2 and BaCrFeAs_2 as obtained from powder neutron diffraction data (instruments E2, E6, and E9 at BER II).

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 $\mu_{\text{Cr}} = 1.9 \mu_B$ is low. Very similar values of T_N and μ_{Cr} have recently been reported for isostructural SrCr_2As_2 and EuCr_2As_2 [9,10]. All these compounds are metallic, in contrast to the corresponding Mn compounds MMn_2As_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 $\mu_{\text{Cr/Fe}} = 1.1 \mu_B$ 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 to the G -type afm structure, suggesting that this Néel-type order is unfavourable for Fe [8]. The question arises whether it is possible to achieve sc starting from these afm Cr compounds?

High-pressure study of BaCr₂As₂ [13]

In a number of Fe-pnictides sc 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 BaCr₂As₂ 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 BaFe₂As₂. In both phases, BaCr₂As₂ is a normal metal. Electronic structure calculations suggest the metallic and afm 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 afm in BaCr₂As₂ and the corresponding Mn compound is in strong contrast to the stripe-type magnetic order typical for BaFe₂As₂ and related compounds and which is easily suppressed, e.g., by a suitable chemical doping.

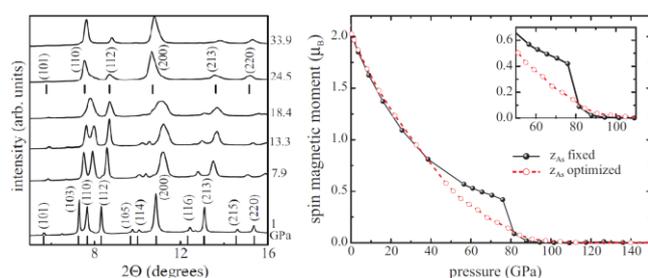


Fig. 2: Left: synchrotron x-ray diffraction patterns of BaCr₂As₂ under high pressure. The peaks are indexed in space group $I4/mmm$. Right: pressure dependence of the calculated spin magnetic moment.

Correlation effects in BaCr₂As₂ – an ARPES study [14]

The electronic structure and especially the strength of electronic correlation in BaCr₂As₂ 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/m_e close to unity for BaCr₂As₂. 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 BaCr₂As₂ (d^3) 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 $3d_{xz/yz}$ hole pockets, in BaCr₂As₂ the $3d_{xy}$ pocket remains below the $3d_{xz/yz}$ 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.

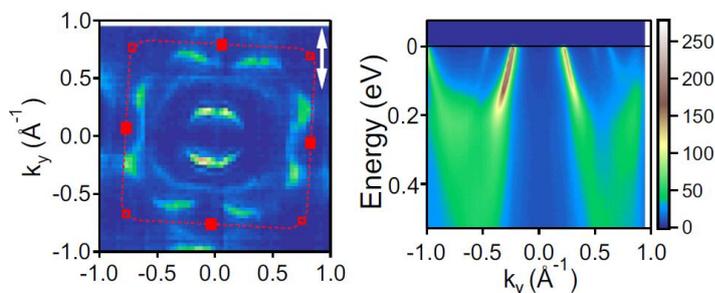


Fig. 3: ARPES intensity (left) and energy-momentum distribution map (right) along $S'-\Gamma-S'$ parallel to k_y using s polarized photons with energy of 70 eV of BaCr₂As₂. The spectra were taken with synchrotron radiation at the BESSY II facility, Berlin.

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