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Magnetic phases in $A_2Cr_3As_3$ alkaline-based materials

GIUSEPPE CUONO

International Research Centre Magtop, Institute of Physics, Polish Academy of Sciences Aleja Lotników 32/46, PL-02668 Warsaw, Poland

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Summary. — We investigate the magnetism in the recently discovered quasi-one dimensional superconductors $A_2Cr_3As_3$ (A=Na, K, Rb or Cs). Since the pressure can be an important tuning parameter that allows to move from the magnetic to the superconducting phase, as found in other chromium-based materials, such as CrAs, here we analyze the role played by the pressure, isotropic or anisotropic, to modify the magnetic properties of these materials. The results we get clarify and shed light on the subtle interplay between magnetism and structural properties of $A_2Cr_3As_3$ compounds.

1. – Introduction

In these years, a great attention has been paid to chromium-based compounds, since they exhibit interesting properties, ranging from magnetism to superconductivity [1]. CrAs compound was the first chromium pnictide that has shown superconductivity under external pressure P [1-8]. It exhibits a dome-shaped T_C *vs.* P similar to cuprates [9], suggesting an unconventional pairing due to the vicinity of the magnetic phase [2, 3, 10]. Since then attempts have been made to find Cr-based superconductors at ambient pressure, and the first compound of this type to be discovered was $K_2Cr_3As_3$ [11-13], with $T_C = 6.1\,\mathrm{K}$. Then, replacing K atom with other alkaline atoms a family of superconducting materials is obtained, with $T_C = 8.6\,\mathrm{K}$ for Na, 4.8 K for Rb and 2.2 K for Cs [14]. These compounds are quasi-one dimensional, and present infinite $[(Cr_3As_3)^{2-}]_\infty$ linear chains of double-walled sub-nanotubes (DWSN), interconnected by A^+ cations, as shown in fig. 1(a) and (b). The lattice is hexagonal with the space group $P\bar{6}m2$ and with the atoms that occupy two planes, one at $z = 0$ and another at $z = 0.5$. Regarding the magnetism, only the *d*-orbitals of the Cr atoms contribute, forming equilateral triangles placed at different planes along the *z*-axis to form a David star. It has been found that this triangular geometry brings to a magnetic frustration, therefore the most stable phase reported is the non-magnetic [15]. Very recently, phonon instabilities were found [16], suggesting that Cr-triangles that are no longer equilateral, and this means that there

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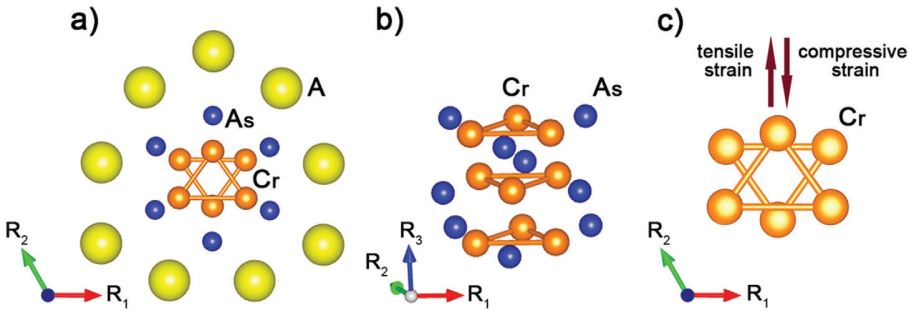


Fig. 1. – (a) Top-view of the crystal structure of the $A_2Cr_3As_3$ (A=Na, K, Rb or Cs) compounds. In case of the replacement of the alkaline element the effect produced on the material is an isotropic pressure. The external and larger radius atoms are the alkaline A elements, the atoms with the smallest radius are the As, while the internal atoms of the nanotubes are the Cr, that are located at the vertices of triangles placed at different planes along the z-axis. These triangles are isosceles if we take into account the distorsions. (b) The double-walled nanotube propagating along the z-direction and formed by Cr and As atoms. (c) We can also apply an uniaxial strain, namely an anisotropic pressure, on the compounds. The strain is applied perpendicular to the basis of the triangles in the chain. The arrows indicate that the strain can be tensile or compressive.

is no more frustration. Thus, it is interesting to investigate the magnetism and what the action of pressure entails. Indeed, the pressure has shown to be an important tuning parameter that allows to move from the magnetic to the superconducting phase, as found in CrAs [2, 3]. Therefore, here we focus on magnetism in the presence of distortions and on what are the changes under the action of a pressure that can be isotropic, as the case of the substitution of the alkaline element A shown in fig. 1(a), or anisotropic, in the case of the action of a uniaxial strain, as shown in fig. 1(c). We report the study of the magnetic ground state for two different cations and under the action of the strain investigated with density functional theory (DFT) calculations. The next section is devoted to the computational details, the results and to the conclusions.

2. – Computational details, results and discussion

We have performed density function theory (DFT) calculations by using the VASP package [17] based on the plane wave basis set and the Projector Augmented Wave method with a cutoff of 440 eV for the plane wave basis and a $4 \times 4 \times 10$ k-point grid. We have used the PBEsol exchange-correlation method [18] and in order to describe the electronic correlations associated with the Cr $3d$ states, a Coulomb repulsion U has been added to our functional.

Taking into account the distortions, we find that the magnetic ground state for values of the Coulomb repulsion $U \geq 0.4$ eV is the collinear up-up-down/up-up-down state, with the spin up on the atoms at the basis of the triangles and the spin down on the atoms at the vertices of the triangle [19]. Instead for $U < 0.4$ eV the ground state is non magnetic, as in the undistorted case. We also get a strong interplay between magnetic and structural properties, therefore as the Coulomb repulsion varies, the sides and the angles of the Cr-triangles vary, and the magnetic moment changes in turn. In fig. 2(a), we report the average magnetic moment of the six chromium atoms of the primitive cell

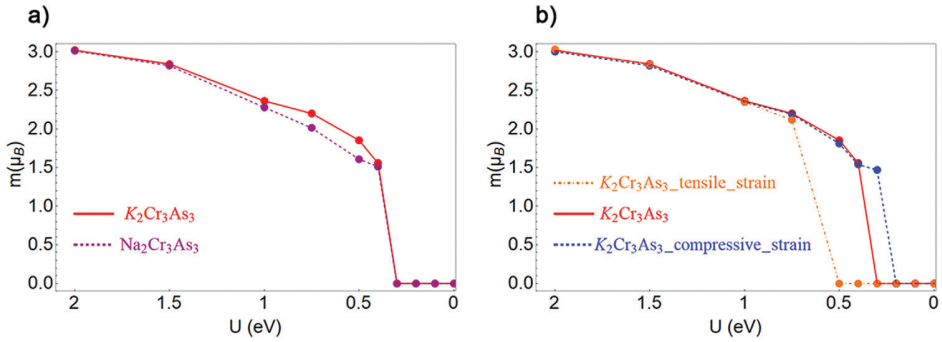


Fig. 2. – (a) Average magnetic moment of the six chromium atoms of the primitive cell as a function of the Coulomb repulsion U for $K_2Cr_3As_3$ (solid line) and $Na_2Cr_3As_3$ (dotted line). (b) Average magnetic moment of the six chromium atoms of the primitive cell as a function of the Coulomb repulsion U for $K_2Cr_3As_3$ without strain (solid line), under a compressive strain with $\epsilon = -0.06$ (dashed line) and under a tensile strain with $\epsilon = +0.06$ (dot-dashed line).

as a function of the Coulomb repulsion U, analyzing the $A_2Cr_3As_3$ in the representative cases of A=K,Na. At high values of the Coulomb repulsion, namely $1.5\,\text{eV} < U < 2\,\text{eV}$ the magnetic moment is large and is close to the saturation value, that is around $3\,\mu_B$. At low values of the Coulomb repulsion the ground state is a non-magnetic configuration, and the magnetic moment goes to zero. We can see that the curves are quite similar, implying that the cation substitution effect is small. The difference between the curves is that the magnetic moment is slightly increasing if we go from Na to K, that is, if we move towards heavier cations.

In fig. 2(b), we report the average magnetic moment of the six chromium atoms of the primitive cell as a function of the Coulomb repulsion U for $K_2Cr_3As_3$ without and with the application of an uniaxial compressive or tensile strain. The lattice vectors of the undistorted unit cell are $\mathbf{R}_1 = (a, 0, 0)$, $\mathbf{R}_2 = (-a/2, \sqrt{3}a/2, 0)$, and $\mathbf{R}_3 = (0, 0, c)$. Under the strain, since the volume is fixed to the value $\frac{\sqrt{3}ca^2}{2}$, we note that the lattice vectors become $\mathbf{R}_1 = (\frac{a}{1+\varepsilon}, 0, 0)$, $\mathbf{R}_2 = (-\frac{a}{2}, \frac{\sqrt{3}a(1+\varepsilon)}{2}, 0)$ and $\mathbf{R}_3 = (0, 0, c)$, where ϵ is $\varepsilon = \Delta a/a$. A negative value of ε corresponds to a compressive strain of the y-component of the $\mathbf{R}_2$ vector, while a positive value corresponds to a tensile one. In fig. 2(b) we apply a compressive strain with $\epsilon = -0.06$ or a tensile strain with ϵ=+0.06 and we compare these cases with the case with vanishing strain. We infer that, differently from the case of the isotropic pressure given by the alkaline element substitution, the action of an uniaxial strain significantly changes the magnetic properties of these materials. In the case of a compressive strain, the magnetic moment goes to zero at a value of the Coulomb repulsion U lower than U when the strain is absent, whereas in the case of tensile strain we observe an opposite trend compared to the previous one. Therefore, according to whether the strain is tensile or compressive, the magnetism can be destroyed or strengthened by means of this structural mechanism. This is due to the fact that the strain modifies the structural properties and consequently the magnetic properties, since these are closely linked together. We point out that this effect is also present when the other alkaline elements of the family are considered. Summarizing, we analyzed the magnetism in the $A_2Cr_3As_3$ compounds in the presence of distortions and under the action of an external pressure, which can be given by the substitution of the cation or

by a uniaxial strain. We remind that this analisys aims to investigate the role played of the isotropic or anisotropic pressure as tuning parameter driving the system towards an ordered magnetic phase. We have seen that the magnetic properties do not vary significantly under the action of an isotropic pressure, but are strongly influenced by an anisotropic pressure such as that given by the strain, which allows to go towards a weakening or strengthening of the magnetism depending on whether the strain is either tensile or compressive. Therefore we are confident that our study turns out to be a reasonable starting point to investigate the action of pressure on stabilizing a magnetic phase and to understand the subtle interplay between magnetism, structural properties and superconductivity in these quasi-one-dimensional compounds.

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