Physica B 481 (2016) 236–243

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Enhanced ferromagnetism induced by structural phase transitions in $Co_2As_{1-x}P_x$

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ARTICLE INFO

Article history:
Received 21 August 2015
Received in revised form
12 November 2015
Accepted 13 November 2015
Available online 1 December 2015

Keywords:
$Co_2As_{1-x}P_x$
Structural phase transitions
Itinerant ferromagnetism
Physical properties
Band structure calculations

PACS numbers:
75.50.Cc
75.10.Lp
75.30.-m

ABSTRACT

P doping in Co_2As induces two structural transitions, resulting in an enhanced ferromagnetic state at intermediate P compositions. In $Co_2As_{1-x}P_x$, doping induces a room temperature α-to-β structural distortion around $x=0.04$, similar to what temperature ($T=725$ K) does in the parent compound ($x=0$). The resulting β phase displays an enhanced ferromagnetic ground state. Close to $x=0.85$, a hexagonal-to-orthorhombic phase transition occurs, concomitant with the quenching of the magnetic order. Band structure calculations for the three different phases confirm the experimental observations while revealing remarkably high charge carrier polarization rate for the β phase.

1. Introduction

Binary M_2Pn or ternary $MM'Pn$ compounds, where M, M'=transition metals and Pn=pnictogen, have attracted intensive interest due to their strong electron correlations and diverse ground states, including magnetism and superconductivity [1–10]. Doping is often associated with structural phase transitions, which, in turn, drive changes to the physical ground state [3,4,9,11]. Co_2As is an example of a M_2Pn hexagonal compound, for which a structural phase transition takes place at $T=725$ K, resulting in an α low temperature phase (Fig. 1a) and a β high temperature phase (Fig. 1b) [2]. Previously reported magnetization measurements show Curie–Weiss-*like* behavior for $T>200$ K, with Weiss temperatures $\theta=-680$ K for the α phase and -430 K for the β phase [2]. Even though these negative θ values suggested antiferromagnetic (AFM) coupling, the extrapolated susceptibility was suggested to be divergent around 10 K, which would indicate ferromagnetic (FM) order in the α phase [2]. However, these conclusions were reached in the absence of low temperature magnetization data (lower than the 80 K [2]) which is needed to study the ground state.

In this study, we show that, at room temperature, P doping in $Co_2As_{1-x}P_x$ induces the α-to-β structural phase transition around $x=0.04$, as well as a hexagonal-to-orthorhombic phase transition for $x>0.85$. After accounting for temperature-independent contributions to the magnetic susceptibility χ_0, magnetization measurements on $Co_2As_{1-x}P_x$ down to $T=2$ K (lower than the 80 K in the previous study [2]) reveal both positive θ values and divergent susceptibility, consistent with FM ground state for the hexagonal phase ($0\le x\le 0.85$). Remarkably, the α-to-β structural phase transition at $x=0.04$ enhances the ferromagnetism in the β phase compared to the α phase. Moreover, the subsequent phase transition at $x>0.85$ quenches the magnetic ground state in the orthorhombic phase. In the orthorhombic phase ($0.95\le x\le 1$), the magnetic susceptibility is temperature-independent when $T>50$ K, consistent with Pauli paramagnetism. The experimental results suggest strong correlations between the crystal structure and the magnetic ground state in $Co_2As_{1-x}P_x$. Band structure calculations for the α and β hexagonal phases, as well as for the orthorhombic phase, confirmed the enhancement of the ferromagnetism in the β-$Co_2As_{1-x}P_x$ phase.

2. Methods

Polycrystalline $Co_2As_{1-x}P_x$ ($0\le x\le 1$) samples were prepared by solid state reaction, in which ground powders of Co (Alfa Aesar, 99.9%), As (Alfa Aesar, 99.99%) and P (Alfa Aesar, 99.999%) were mixed in the ratio of Co:As:P=1.95: $1-x$:x and sealed in

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http://dx.doi.org/10.1016/j.physb.2015.11.016
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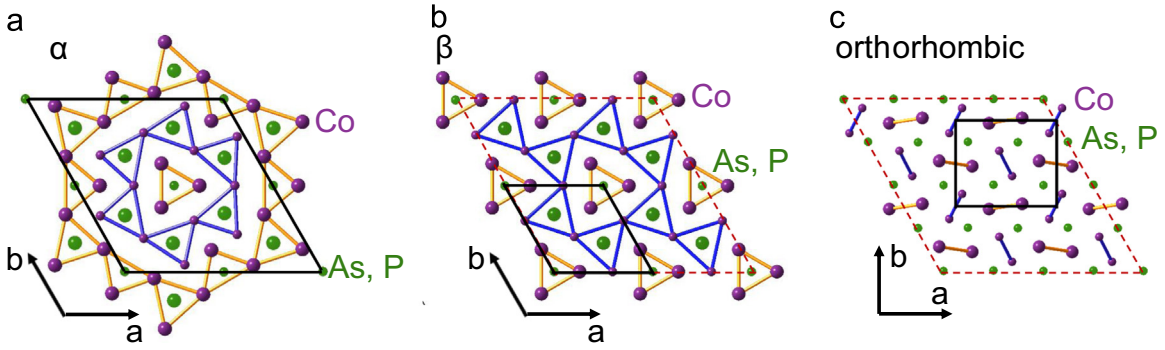

Fig. 1. $Co_2As_{1-x}P_x$ crystal structure for (a) the hexagonal α phase, (b) the hexagonal β phase, and (c) the orthorhombic phase. The unit cell is indicated by the black solid line, and the red dashed parallelograms are used as a comparison with the hexagonal α phase. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

evacuated quartz tubes. The samples were heated between 400 °C and 900 °C for six days, with intermediate grindings. Room temperature powder x-ray diffraction (XRD) measurements were performed on a Rigaku D/Max diffractometer with Cu Kα radiation and a graphite monochromator. Rietveld analysis was done using the GSAS suite of programs [12]. Temperature- and field-dependent magnetization data were collected in a Quantum Design (QD) Magnetic Property Measurement System (MPMS) for temperatures between 2 K and 300 K and applied magnetic field H up to 7 T. DC resistivity measurements were performed in a QD Physical Property Measurement System (PPMS) using a standard four-probe method. Specific heat measurements were also performed in the QD PPMS using an adiabatic relaxation technique.

Band structure calculations within the density functional framework were performed using a full potential linear augmented plane wave method (FP-LAPW), as implemented in the WIEN2k code [13]. A cutoff parameter $RK_{max} = 7.0$ was used, and the exchange-correlation potential was taken in the commonly used Perdew–Burke–Ernzerhof (PBE) form [14] of the generalized-gradient approximation. The linear tetrahedron method was employed for the Brillouin zone (BZ) integration, with the k-mesh of $10 \times 10 \times 10$ points in the primitive BZ. Both paramagnetic (PM) and ferromagnetic (FM) density of states (DOS) are calculated for α-Co_2As, β-Co_2As and Co_2P.

3. Experimental results

The Co_2As crystal structure consists of different Co (As) sites, six (five) in the hexagonal α phase, two (two) in the hexagonal β phase, and two (one) in the orthorhombic phase, with the atoms in the $z=0$ (0.5) plane represented by the larger (smaller) spheres in Fig. 1. The hexagonal structure with space group $P\bar{6}2m$ [11] persists up to 1313 K, with a structural distortion around 725 K. In the low temperature α phase ($T \leq 725$ K, Fig. 1a), the Co atoms in different planes form rings of distorted triangles, centered around As atoms in planes half a unit cell above and below. At $T=725$ K, the Co atoms move to higher symmetry positions (Fig. 1b), resulting in the high temperature hexagonal β phase. While this crystallographic modification preserves the same space group, the a and b unit cell parameters (outlined in black) are nearly half when compared to those of the α phase [2].

This high temperature β phase appears to also be stabilized at room temperature by P doping. P doping changes the room temperature crystal structure of $Co_2As_{1-x}P_x$ from the low temperature α phase to the high temperature β phase when $0.06 \leq x \leq 0.85$, while the α phase is preserved for lower x values. Further P doping induces a structural phase transition from the hexagonal $P\bar{6}2m$ to an orthorhombic structure with space group $Pnam$ (Fig. 1c) for

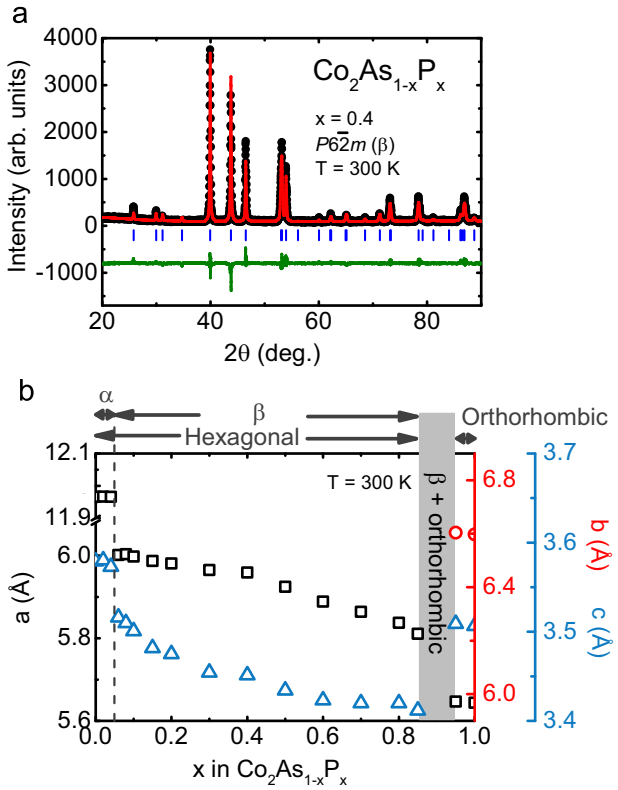

Fig. 2. (a) Rietveld refinement profile for the room temperature XRD data for $Co_2As_{0.6}P_{0.4}$. The difference between measured data (black) and Rietveld fit (red) is shown as a green line. The calculated Bragg peak positions for $Co_2As_{0.6}P_{0.4}$ are indicated by blue vertical markers. (b) Lattice parameters of $Co_2As_{1-x}P_x$ as a function of x. Error bars are smaller than the symbol size. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

$0.95 \leq x \leq 1$. $Co_2As_{1-x}P_x$ forms mixed phases and no single phase was observed for $0.85 < x < 0.95$. The Rietveld refinement of the $Co_2As_{1-x}P_x$ room temperature powder XRD patterns, with an example shown in Fig. 2a for $x=0.40$, confirms the structure and purity. The lattice parameters for $Co_2As_{1-x}P_x$ as a function of x are shown in Fig. 2b, and are close to previously reported values [4,11]. Initially, P doping in $Co_2As_{1-x}P_x$ leaves the lattice parameters virtually unchanged in the α phase, for $x \leq 0.04$. An α-to-β structural transition occurs between $x=0.04$ and 0.06, with both the a (squares, left axis) and c (triangles, right axis) lattice parameters changing abruptly (Fig. 2b). Upon further increasing the amount of P in place of the larger As atoms, a monotonic decrease of the lattice parameters is observed for $0.06 \leq x \leq 0.85$ (Fig. 1b),