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Study of Ni and Zn doped CeOFeAs: Effect on the structural transition and specific heat capacity

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ABSTRACT

We have systematically studied the substitution of nonmagnetic Zn and magnetic Ni at iron sites in Ce based oxypnictide. The parent compound (CeOFeAs) shows an anomaly in resistivity around 150 K due to structural transition from tetragonal (space group: *P4/nmm*) to orthorhombic structure (space group: *Cmma*). Substitution of Zn suppresses this anomaly to lower temperature ($\sim$130 K) but Ni substitution does not show any anomaly around this temperature and the compound behaves like a metal. Further, we find that non magnetic (Zn) doping leads to higher impurity scattering as compared to magnetic Ni doping. Similar to the resistivity measurement, the specific heat shows another jump near 4 K for CeOFeAs. This is attributed to the ordering of Ce^{3+} moments. This peak shifts to 3.8 K for Zn substituted compound and there is no change in the ordering temperature in the Ni substituted CeOFeAs. These peaks are broadened in applied magnetic field (5 T) and the calculated magnetic entropy tends to saturate at the same value for 0 T and 5 T external magnetic field.

1. Introduction

The main structural feature of the iron–arsenic based superconductor (REOFeAs; RE = rare earth) is the FeAs planes. The parent compound of these iron pnictides are antiferromagnets [1] similar to cuprate based high temperature superconductors. These compounds have a tetragonal structure and show superconductivity after suitable substitution [1–4]. Many studies have been reported on the doping at various sites of REOFeAs. In some cases the transition temperature and upper critical field increase while doping of certain ions lead to impurity scattering and pair breaking that do not support the superconducting phases.

The emphasis of current discussion in these new superconductors is the origin of the superconducting pairing mechanism. Theoretical studies suggest that the pairing may be realized via inter-pocket scattering of electrons between the hole and electrons pockets, giving rise to a multiband s-wave pairing with possible sign change of the superconducting gap on the Fermi surface (so called s ± gap) [5–7]. Some other models have suggested that the pairing mechanism has its origin in magnetic super exchange [8–9] with multiband s-wave pairing. Further, it has also been established that if the height of pnictogen from Fe-plane is varied, the pairing symmetry could effectively be changed from s-wave to d-wave symmetry [10]. The experimental results are equally controversial. While some experiments support the s ± symmetry, some other reflects d-wave symmetry [11–17]. These controversies have necessitated the study of impurity scattering and pair breaking through magnetic and non-magnetic doping in the oxypnictides in greater detail.

In this context, Anderson model suggests that while in conventional s-wave superconductors the non-magnetic dopant would not lead to pair breaking [18], in d-wave superconductors (as seen in cuprates), the substitution of such impurities could lead to rapid suppression of superconductivity [19]. For example, it is now established that doping of non-magnetic Zn^{2+} in cuprates, suppresses the transition temperature more effectively in comparison to magnetic impurities like Mn or Co [20]. With regard to ferropnictides, band structure calculations [21] suggest that the iron based superconductors have itinerant behavior of Fe 3d electrons. In contrast, the copper (Cu) 3d electrons have localized behavior in cuprate superconductors. Based on these ideas, we have reported the substitution of cobalt at iron sites in CeOFeAs to introduce extra electrons and induce superconductivity in Co-doped CeOFeAs [22]. Superconductivity is also observed in nickel doped LaOFeAs [23]. Li et al. [24] have shown that the substitution of nonmagnetic Zn ions (up to $\sim$10%) at iron sites does not affect the transition temperature of 10% F-doped LaOFeAs. On the contrary similar study by Guo et al. has indicated large decrease in T_c of LaOFeAs with 3% Zn doping [25]. Further, no such study on Ce based ferropnictides has been reported. This is of interest because unlike the LaOFeAs, the parent Ce-based oxypnictide shows two

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antiferromagnetic transitions one around 150 K due to Fe 3d electrons, and the other around 4 K due to ordering of Ce^{+3} ions. In this paper, we have studied the effect of partial substitution of the non-magnetic Zn and magnetic Ni ions at iron sites in CeOFeAs and have investigated its structural, electronic and magnetic properties. Our result suggests that the substitution of non-magnetic ions generate higher disorder induced impurity scattering as compared to magnetic ion doping.

2. Experiments

For the synthesis of $CeOFe_{1-x}M_xAs$ (M = Ni and Zn), high purity Ce, As, CeO_2, Ni, ZnO, and FeAs were used. FeAs was obtained by heating stochiometric amounts of Fe chips and As powder in an evacuated silica tube at 595 °C for 12 h followed by heat treatment at 630 °C for 12 h and finally heated at 800–900 °C for 24 h. The rare earth oxides were preheated at 900 °C before weighing. The reactants were weighed according to the stoichiometric ratio in a N_2-filled glove-box and then sealed in evacuated silica ampoules (10^{-4} torr) and heated at 950 °C for 48 h at a rate of 50 °C/h. The resulting powder was compacted into disks under 5 ton pressure. The disks were wrapped in Ta foil, sealed in evacuated silica ampoules and annealed at 1150 °C for 48 h at a rate of 100 °C/h and then cooled to room temperature. Powder X-ray diffraction patterns of the finely ground powders were recorded with Cu Kα radiation in the 2θ range of 20°–70°. The lattice parameters were obtained from a least squares fit to the observed *d* values.

Resistivity measurement was carried out using a Cryogenic 8 T Cryogen-free magnet in conjunction with a variable temperature insert (VTI). The samples were cooled in helium vapor and the temperature was measured with an accuracy of 0.05 K using a calibrated Cernox sensor wired to a Lakeshore 340 temperature controller. Standard four probe technique was used for transport measurements. The external magnetic field (0–5 T) was applied perpendicular to the probe current direction and the data were recorded during the warming cycle with heating rate of 1 K/min. The magnetic and specific heat measurements were carried out on Quantum design Physical property Measurement System (PPMS).

3. Results and discussion

Powder X-ray diffraction patterns for Ni substituted $CeOFe_{1-y}Ni_yAs$ ('*y*' = 0, 0.1 and 0.2) are shown in Fig. 1a. All observed reflections could be satisfactorily indexed on the basis of tetragonal crystal structure (space group: *P*4/*nmm*). The variation of lattice parameters (a and c) with nickel substitution is shown in Fig. 1b. The *c*-lattice parameter decreases with increase in nickel substitution which is expected since the ionic size of Ni^{2+} (0.55 Å) is smaller as compared to Fe^{2+} (0.63 Å) in tetrahedral coordination. The variation of a-lattice parameter with Ni doping is not systematic. For '*y*' = 0.1 composition, a slight decrease in *a*-lattice parameter is observed while the '*y*' = 0.2 composition has approximately the same a-lattice parameter as for '*y*' = 0 composition. The *c*/*a* ratio and volume of tetragonal cell also shrinks on Ni doping in $CeOFe_{1-y}Ni_yAs$. Cao et al. [23] also reported reduction in *c*-lattice parameter, *c*/*a* ratio and volume of cell on Ni substitution in LaOFeAs.

Powder X-ray diffraction patterns of Zn doped $CeOFe_{1-x}Zn_xAs$ ('*x*' = 0, 0.15, 0.2) are shown in Fig. 1c. For '*x*' = 0.15 compositions,

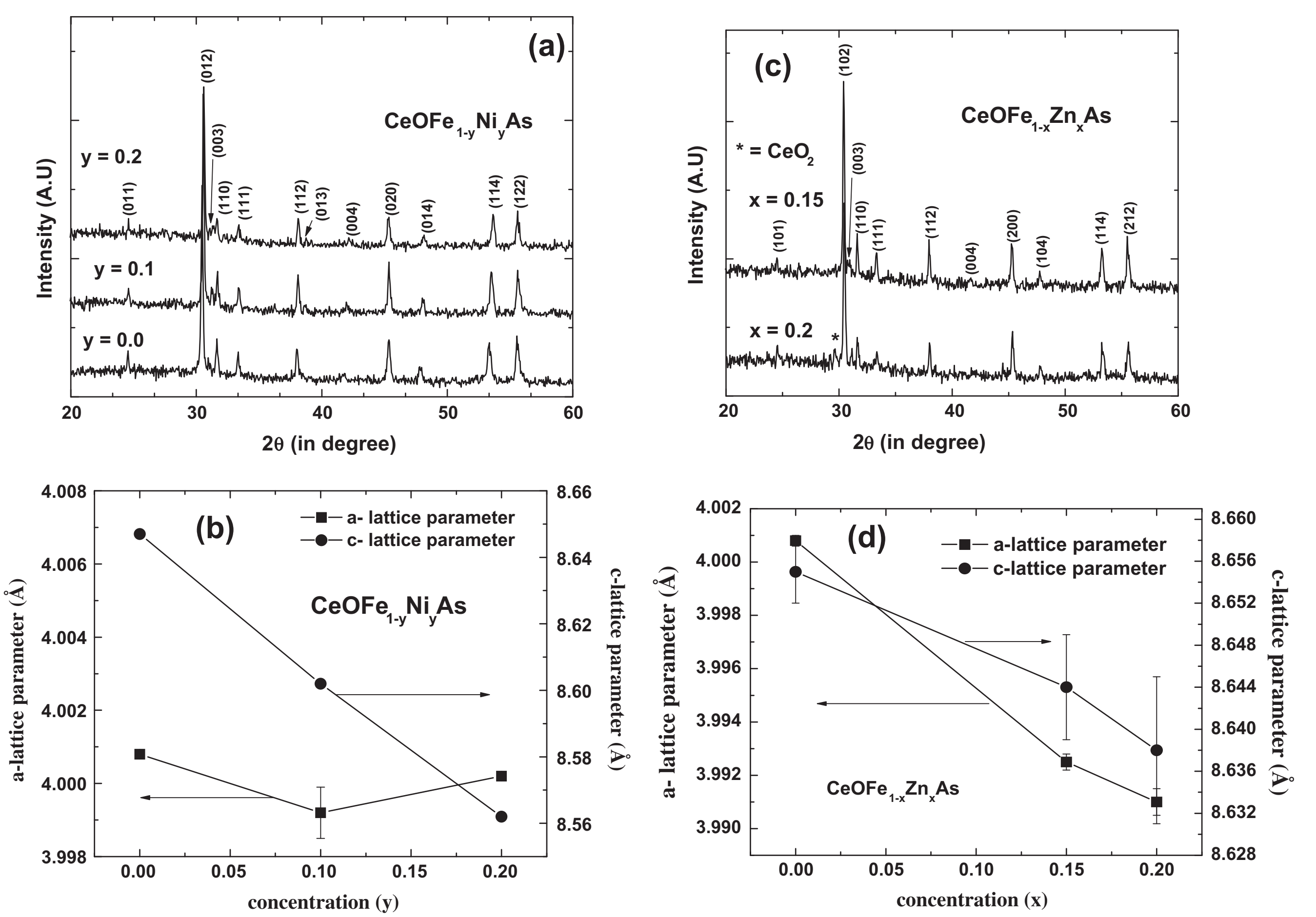

Fig. 1. (a) Powder X-ray diffraction (P-XRD) patterns and (b) variation of lattice parameters ('a' and 'c') for $CeOFe_{1-y}Ni_yAs$ (y = 0, 0.1 and 0.2). (c) PXRD patterns and (d) variation of lattice parameters ('a' and 'c') for $CeOFe_{1-x}Zn_xAs$ (x = 0.15 and 0.2).