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Calorimetric study of the superconducting and normal state properties of $Ca(Fe_{1-x}Co_x)_2As_2$

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Abstract. We present a calorimetric study on single crystals of $Ca(Fe_{1-x}Co_x)_2As_2$ (x = 0, 0.032, 0.051, 0.056, 0.063, and 0.146). The combined first order spin-density wave/structural transition occurs in the parent $CaFe_2As_2$ compound at 168 K and gradually shifts to lower temperature for low doping levels (x = 0.032 and x = 0.051). It is completely suppressed upon higher doping $x \geq 0.056$. Simultaneously, superconductivity appears at lower temperature with a transition temperature around $T_c \sim 14.1$ K for $Ca(Fe_{0.937}Co_{0.063})_2As_2$. The phase diagram of $Ca(Fe_{0.937}Co_{0.063})_2As_2$ has been derived and the upper critical field is found to be $\mu_0 H_{c2}^{(c)} = 11.5$ T and $\mu_0 H_{c2}^{(ab)} = 19.4$ T for the c and ab directions, respectively.

1. Introduction

After the discovery of superconductivity in LaFeAsO (1111 compound) with a transition temperature $T_c \sim 26$ K [1], a lot of investigations have been undertaken finding an increase of T_c by replacing La with smaller size rare earth ions [2] reaching up to $T_c = 55$ K in $SmO_{1-x}F_xFeAs$ [3]. Simultaneously, several other families of Fe-based layered superconductors have been discovered, such as the $ThCr_2Si_2$ structure-type AFe_2As_2 (122 family, A = Ca, Sr, Ba, Eu). They adopt a structure analogous to oxypnictides with LaO layers replaced by layers of A. These series are of great interest because large single crystals can be grown [4] which show a structural transition from a tetragonal to an orthorhombic structure combined with an antiferromagnetic ground state due to a spin-density wave (SDW) formation [5]. Furthermore, the parent compound of the 122 series becomes superconducting upon electron and hole doping [6],[7]. The $CaFe_2As_2$ system is of particular interest because the application of a pressure of 0.69 GPa is sufficient to suppress the SDW/structural transition completely and to induce superconductivity with a T_c exceeding 10 K [8],[9] while for $SrFe_2As_2$ and $BaFe_2As_2$ higher pressure up to 4 GPa are needed [10]. We should also mention that the electron and hole doped $BaFe_2As_2$ and $SrFe_2As_2$ series of compounds have remained very much in focus, while studies on the analogous $CaFe_2As_2$ compounds are very scarce.

Since specific heat measurements can provide useful information about the electronic and the gap structural properties, it is important to explore the normal state and

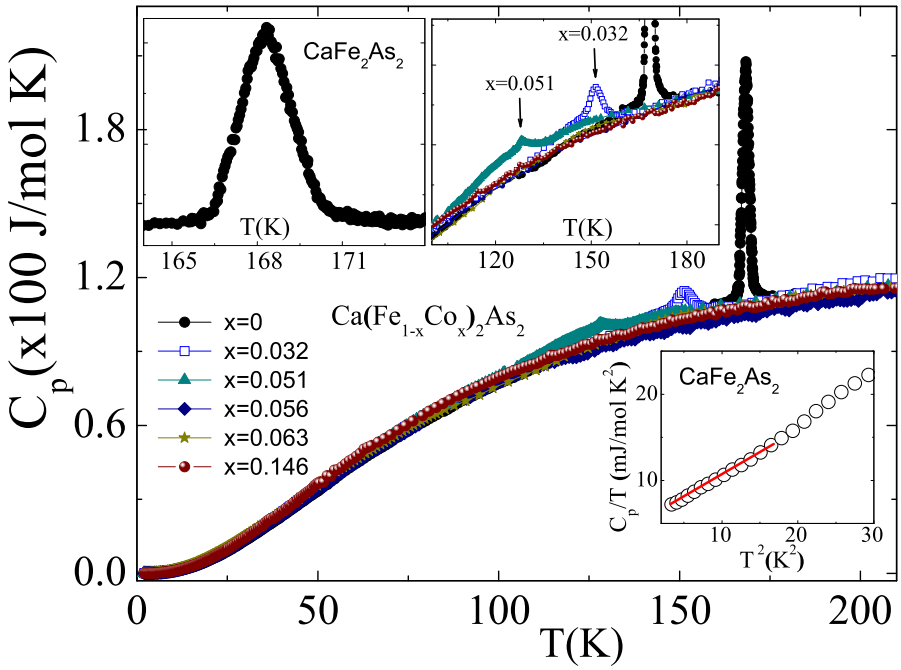

Figure 1. Temperature dependence of the specific heat of $Ca(Fe_{1-x}Co_x)_2As_2$ for $x = 0$, 0.032, 0.051, 0.056, 0.063, and 0.146 measured in zero magnetic field. The lower inset depicts the low temperature specific heat of the parent $CaFe_2As_2$ compound together with a fit to $C_p = \gamma T + \beta T^3$ shown as a red solid line. The upper insets show a zoom into the region around the phase transition for $CaFe_2As_2$ plotted as C_p vs. T and upon Co doping.

superconducting properties of $Ca(Fe_{1-x}Co_x)_2As_2$ single crystals using this technique. In this contribution, we present a first calorimetric study of both antiferromagnetic and superconducting $Ca(Fe_{1-x}Co_x)_2As_2$ for ($x = 0$, 0.032, 0.051, 0.056, 0.063 and 0.146) and report on the superconducting properties of the $Ca(Fe_{0.937}Co_{0.063})_2As_2$ single crystal.

2. Experimental

Single crystals of $Ca(Fe_{1-x}Co_x)_2As_2$ were grown by the high temperature solution growth method using Sn flux. All room-temperature processing (weighing, mixing, grinding and storage) of these materials was carried out in an Ar filled glove-box (O_2 and moisture level less than 0.1 ppm). The crystal growth and the physical properties of the $Ca(Fe_{1-x}Co_x)_2As_2$ series are presented in details in ref.[4],[11]-[15] and the x values are indicating the composition as measured by Energy-dispersive X-ray spectroscopy (EDX) [4]. The specific heat measurements have been performed in a Physical Property Measurement System (PPMS) using a relaxation technique. For the measurements $B \parallel ab$ a small copper block has been used to mount the sample on the specific heat puck. The heat capacity of the copper block was determined in a separate measurement and directly subtracted. A temperature rise of only 0.5 % was used for those measurements in the vicinity of the transition of the un-doped sample.

3. Results and discussions

Fig. 1 summarizes the temperature dependence of the zero-field specific heat at various Co-doping of $Ca(Fe_{1-x}Co_x)_2As_2$ between 1.8 and 220 K. In the parent compound ($x = 0$) a sharp first-order structural transition coincides with a SDW transition at $T_s = 168$ K (upon warming), which is in a good agreement with literature [4],[12],[16]. The transition width is estimated to

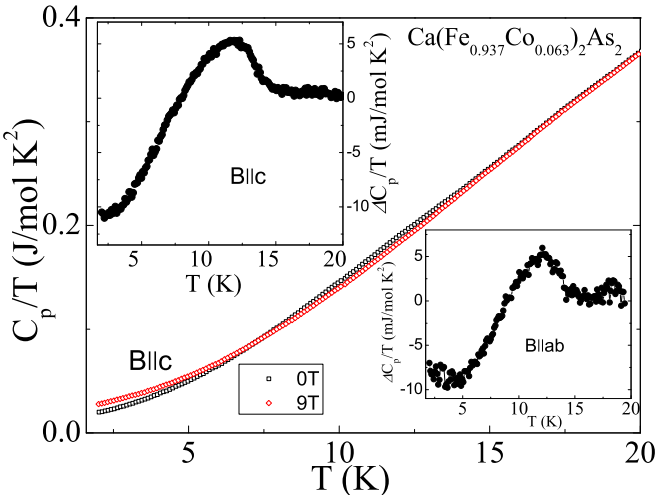

Figure 2. Specific heat measurements of $Ca(Fe_{0.937}Co_{0.063})_2As_2$ measured in zero and 9 T for $B \parallel c$. The upper inset shows the difference between the zero and 9 T data, $\Delta C_p/T$, which depicts a specific heat jump with a superconducting transition temperature of about 14.1 K for $B \parallel c$. The lower inset shows the difference between the zero and 9 T data, $\Delta C_p/T$, for $B \parallel ab$.

be about 4 K. To determine the Sommerfield coefficient γ of our $CaFe_2As_2$ single crystal, the low-temperature specific heat data are plotted as C_p/T as a function of T^2. These data can be fitted to a $C_p = \gamma T + \beta T^3$ power law, where γ and β are determined by the electronic and phononic contributions, respectively, as shown in the lower inset in Fig. 1. The γ value is found to be around 5.4 mJ/mol K^2, which is in agreement with values ranging between 4.7 - 8.2 mJ/mol K^2 in the literature [5],[16]. At present we do not understand this relatively large sample dependent variation in the measured values of γ. It is, however, conceivable that this difference is due to a different single crystal growth technique which is leading to differences in the crystal quality. The phononic coefficient β is found to be ~ 0.508 mJ/mol K^4. Using the relation $\theta_D = (12\pi^4 RN/5\beta)^{1/3}$, where R is the molar gas constant and $N = 5$ is the number of atoms per formula unit, we obtain the Debye temperature $\theta_D = 267$ K.

Upon Co doping of the system the combined SDW/structural transition is shifted to lower temperature and becomes broader and considerably reduced in magnitude, with the transition being shifted to 148 K and 128 K for $x = 0.032$ and $x = 0.051$, respectively, as shown in the upper inset in Fig. 1. Contrary to the magnetization, resistivity and neutron diffraction studies [4],[15], in our specific heat studies no evident splitting of the structural and magnetic transition was found in our sample $x = 0.051$ and $x = 0.056$. For higher Co doping the transitions are completely suppressed and superconductivity evolves at low temperature. The transitions observed in the specific heat data are in general consistent with those found in the resistivity, magnetization and neutron diffraction [4],[11],[15] measurements performed in few of $Ca(Fe_{1-x}Co_x)_2As_2$ single crystals from the same batch like those used in the present study.

Figure 2 shows the temperature dependence of the heat capacity of $Ca(Fe_{0.937}Co_{0.063})_2As_2$ in zero and 9 T for $B \parallel c$. Taking into account the relatively broad superconducting transition in both resistivity and susceptibility measurements on the same single crystal as discussed in detail in [4], the apparent lack of the anomaly at T_c may be due to the relatively large transition width. This is strongly supported by specific-heat data on superconducting $CaFe_{1.94}Co_{0.06}As_2$ single crystals, where no superconducting transition has been observed either [17]. This probably reflects the presence of nanoscopic inhomogeneities intrinsic to the Ca-system which is beyond the detection limit of EDX or we can speculate that the broad nature of superconducting transitions is related to the extreme pressure sensitivity of this compound.

However, in order to obtain information about the electronic properties in the superconducting state, we subtracted our 9 T specific heat data from the zero-field data for

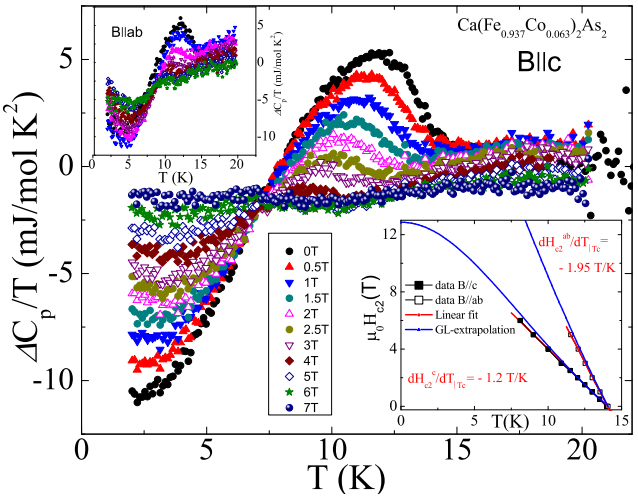

Figure 3. Specific heat data $\Delta C_p/T = C_p(B) - C_p(9T)$ of $Ca(Fe_{0.937}Co_{0.063})_2As_2$ in various magnetic fields for $B \parallel c$. The upper inset shows $\Delta C_p/T$ for $B \parallel ab$. The lower inset depicts the phase diagram estimating the upper critical fields, where the blue dotted lines show the theoretical curves based on the G-L theory and the red dotted lines represent linear fits with average slopes of $-\mu_0 dH_{c2}^{(c)}/dT = 1.2$ T/K and $-\mu_0 dH_{c2}^{(ab)}/dT = 1.95$ T/K for the c and ab directions, respectively.

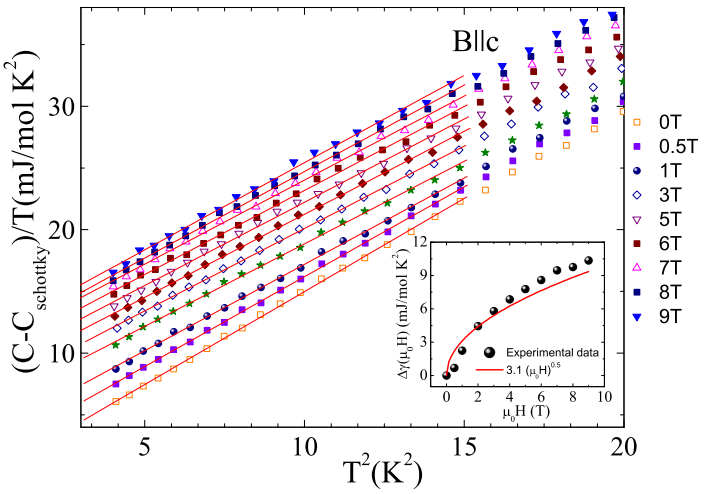

Figure 4. The electronic specific-heat coefficient C_p-$C_{Schottky}$/T vs. T^2 of $Ca(Fe_{0.937}Co_{0.063})_2As_2$ for magnetic fields $B \parallel c$ up to 9 T. The data show a rather linear behavior is detected after subtracting the Schottky contribution (in the form $c_p = \gamma T + AT^{-3}$) to the specific heat at low temperatures. Solid red lines are represent linear fit in the form $C_p = \gamma T + \beta T^3$ (see table 1). The lower inset depicts the field dependence of $\Delta\gamma(H)$ for $B \parallel c$. The solid red line represents a fit to $\Delta\gamma(H) = A(\mu_0 H)^{0.5}$.

both directions, labeled as $\Delta C_p/T$ in the insets of Fig. 2. The extracted superconducting transition temperature is found to be 14.1 K, which is in agreement with resistivity and magnetization studies on single crystals from the same batch [4],[11]. Note, that this analysis for the estimation of the transition temperature T_c can be applied since the superconducting transition of $Ca(Fe_{0.937}Co_{0.063})_2As_2$ is strongly suppressed and shifted to lower temperaturesin in an external magetic field of 9T. The same procedure has been used to extract T_c for other fields up to 6 T (shown in Fig. 3) using the half jump height. From Fig. 3 it can be clearly seen that the superconducting transition is systematically shifted to lower temperature and reduced in height with increasing magnetic field. This behavior occurs for both field directions.

From the field dependence of T_c the phase diagram of $Ca(Fe_{0.937}Co_{0.063})_2As_2$ can be drawn, which is shown in the lower inset of Fig. 3 depicting the experimental data as well as the estimated upper critical field values H_{c2} for both directions. According to the Ginzburg-Landau (GL) equation [18], H_{c2} can be expressed as

$$H_{c2}(t) = H_{c2}(0)[\frac{1-t^2}{1+t^2}], \quad (1)$$

where t is the reduced temperature $t = T/T_c$. The upper critical field at $T = 0$ has been evaluated to be $\mu_0 H_{c2}^{(c)}(0) = 12.7$ T and $\mu_0 H_{c2}^{(ab)}(0) = 25.4$ T for the c and ab direction,

Table 1. Fitting parameters of the low temperature specific heat data of $CaFe_{0.937}Co_{0.063}As_2$ single crystals using $C_p = \gamma T + \beta T^3$ after subtracting the Schottky contribution.

μ_0(H)	γ	β
(T)	(mJ/mol K^2)	(mJ/mol K^4)
0	0.945	1.51
0.5	1.63	1.46
1	3.19	1.4
2	5.49	1.34
3	6.74	1.34
4	7.8	1.34
5	8.73	1.35
6	9.57	1.36
7	10.41	1.36
8	10.71	1.4
9	11.3	1.4

respectively. Another possibility to extract the upper critical field is to consider the single-band Werthamer-Helfand-Hohenberg (WHH) model [19]:

$H_{c2}(0) = -0.69\, T_c (dH_{c2}/dT)_{T_c}$. Our data are perfectly described by a linear fit to the WHH model with an average slope $-\mu_0 dH_{c2}/dT = 1.2$ T/K and 1.95 T/K yielding upper critical fields $\mu_0 H_{c2}(0) = 11.5$ T and 19.4 T for the c and ab direction, respectively. Note, that resistivity studies on $CaFe_{1.94}Co_{0.06}As_2$ single crystals show similar values for the average slopes, i.e., $-\mu_0 dH_{c2}{}^{(c)}/dT = 1.4$ T/K for B $\parallel$ c and $-\mu_0 dH_{c2}{}^{(ab)}/dT = 1.8$ T/K for B $\parallel$ ab [17].

Figure 4 depicts the low temperature specific heat of $Ca(Fe_{0.937}Co_{0.063})_2As_2$ plotted as C_p-$C_{Schottky}$/T vs. T^2 in different applied magnetic fields for $B \parallel c$. One can see the roughly linear behavior after subtracting the Schottky contribution (in the form $C_p = \gamma T + AT^{-3}$) to the specific heat at low temperatures. A similar approach was successfully applied in the case of $Sr_3Ru_2O_7$ to subtract the Schottky contribution has been reported by *Zhou et al.*, [21]. It is clear that the magnetic field enhances the low-temperature specific heat continuously, indicating the increase of the quasiparticle density-of-states at the Fermi level induced by a magnetic field. A linear extrapolation of the low-T data to zero temperature yields the field dependence of the field-induced contribution (the values of the electronic and phnonic contributions are shown in table 1).

$$\Delta\gamma(H) = [C(T,H) - C(T,0)]/T. \quad (2)$$

The lower inset of Fig. 4 shows $\Delta\gamma(H)$ for $B \parallel c$, clearly indicating a non-linear behavior in magnetic fields. In fact, this non-linear behavior can be fitted by the simple equation $\Delta\gamma(H) = A(\mu_0 H)^{0.5}$ predicted for d-wave symmetry in the clean limit [20]. One can see that the theoretical curve can not describe the whole data. In the case of $Ba(Fe_{1-x}Co_x)_2As_2$ single crystal at (x = 0.045, 0.08, 0.103, and 0.105), the $\gamma(H)$ values of the low-temperature specific heat data can not be described by a single s-wave gap [22]. However, it is difficult to solely judge from specific heat data wether nodes exist or not and it should be noted that other pairing mechanisms can also result in a non-linear behavior of $\gamma(H)$.

4. Conclusions

In summary, we have studied the heat capacity of single crystals of $Ca(Fe_{1-x}Co_x)_2As_2$ ($x = 0$, 0.032, 0.051, 0.056, 0.063, and 0.146). Here, a combined magnetic and structural ordering has been observed for the parent compound evidenced by a first order transition around 168 K. For higher doping levels this transition shifts to lower temperatures, until it is completely suppressed for x = 0.056 and superconductivity appears around 14.1 K. From the low temperature specific heat data of the Co-doped superconducting $Ca(Fe_{0.937}Co_{0.063})_2As_2$ single crystal, the upper critical field has been determined using the WHH model. It is found to be 11.5 T and 19.4 T for $B \parallel c$ and $B \parallel ab$, respectively. A non-linear behavior of the field dependence of $\gamma(H)$ in the low-temperature region after substracting the Schottky contribution to the specific heat.

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