

On the phase diagram of $\text{CrAs}_{1-x}\text{Sb}_x$

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Abstract. Transport, magnetic, XRD and XPS studies have been performed on $\text{CrAs}_{1-x}\text{Sb}_x$ in an effort to obtain the phase diagram in the intermediate range ($x \sim 0.5$) in the hexagonal phase. We found that CrAs undergoes antiferromagnetic and structure transition at $T_N = 240\text{K}$. Upon Sb substitution ($x > 0.3$), the Neel temperature is sharply suppressed with slope $(-10.7 \frac{\text{K}}{x} \%)$ in much similar way to the suppression caused by pressure in CrAs single crystal. The chemical compositions obtained using XPS are in good agreement with nominal values. Moreover, XPS reveals no changes in the valance states for the constituent elements of $\text{CrAs}_{1-x}\text{Sb}_x$. Unexpectedly, we found that arsenic at the surface has higher atomic ratio than the nominal composition. This may be due to segregation of arsenic to the surface of sample.

1. Introduction

Recent discovery of superconductivity in CrAs under high pressure (10 kbar) opened new possibility in discovering superconductivity in other transition metal based pnictide [1,2]. At ambient pressure, CrAs is non-superconductor. CrAs belongs to a large family of MX compounds where M is a transition metal and X is P , As or Sb , and has "commonly" orthorhombic structure [3,4]. Its magnetic, transport and structural properties were studied extensively in the seventies and eighties of twentieth century in an effort to probe the magnetic and semiconducting properties. It is well established that CrAs undergoes first order antiferromagnetic transition at Neel temperature (T_N). Most of the previous magnetic, structural and transport properties were investigated above liquid nitrogen temperature [3,4]. The Neel and the structure transition temperatures were continually suppressed with increasing pressure [1,2].

In this work, we investigated the phase diagram of $\text{CrAs}_{1-x}\text{Sb}_x$, in the intermediate region of the phase diagram ($x \sim 0.5$) where the Neel temperature reaches its minimum value. We use transport and XPS analyses to investigate the variation of T_N with Sb substitution and the electronic states of Cr , As and Sb .

2. Experimental method

Solid state reaction was used to prepare $\text{CrAs}_{1-x}\text{Sb}_x$ with $x = 0.00, 0.45, 0.50, 0.60$ and 0.65 . Stoichiometric ratios of high purity (99.99%) powders of Cr , As and Sb were mixed, ground and pressed into pellets under $\sim 3 \text{ Ton/cm}^2$ then sealed in quartz tubes under partial argon pressure. To reduce the volatility of As and Sb during annealing, all samples were heated slowly ($\sim 60^\circ\text{C/h}$) to 600°C and annealed for 10 hours. The temperature was raised slowly ($\sim 60^\circ\text{C/h}$) to 1100°C and annealed for 24 hours. The temperature was reduced to 900°C and was kept for 72 hours. Finally, the samples were annealed at 300°C for another 72 hours, and then quenched to room temperature.



The resistance was measured in a temperature range 4-300K using four probes ac resistance bridge (LR-750) operating at 16Hz. The temperature was monitored using Lake Shore-336 temperature controller along with closed cycle refrigerator (Model SHI-4T). LABVIEW software was used to control all measuring systems and collect the data. The XPS analysis was performed using a Thermo-Scientific (Escalab-250 Xi). The elemental composition and the oxidation state of all elements (Cr, As and Sb) in each sample were obtained by this technique.

3. Results and discussions

3.1. XRD analysis

patterns for all samples were analyzed using MAUD software. The CrAs structure is orthorhombic with lattice parameter $a = 6.2082 \text{ \AA}$, $b = 5.6519 \text{ \AA}$ and $c = 3.4691 \text{ \AA}$. For $x \geq 0.45$; the structure becomes hexagonal, with traces of the orthorhombic phase. In the hexagonal phase both lattice parameters a and b shrink dramatically reduced to 3.6932 \AA , while the lattice parameter c ; elongates considerably from 3.4793 to 5.7651 \AA . Our results are consistent with earlier studies reported [3-4].

3.2. XPS analysis

The electronic state and chemical composition of the $\text{CrAs}_{1-x}\text{Sb}_x$ samples were obtained using XPS. The spectra of all elements in each sample along with deconvoluted peaks are analyzed. A representative data for CrAs sample is shown in figure 1. Chromium $2p$ core level spectrum shows multiplet splitting due to unpaired d - electrons, in addition to spin-orbit splitting ($2p_{3/2}$ and $2p_{1/2}$). The binding energy for $\text{Cr } 2p_{3/2}$ is assigned to the alloy and the valence state is Cr^{+3} . Similarly, arsenic and antimony $3d$ core level spectra also consist of spin-orbit doublets. The binding energy of $\text{As } 3d_{5/2}$ is assigned to alloy and the valence state is As^{-3} . Unexpectedly, arsenic composition is found higher than the nominal value, indicating that arsenic segregates to the surface of the sample. However, using depth profile analysis, we found that the overall concentration of As and Sb agrees within 5-10% of the nominal concentration.

3.3. Transport measurements

The measured resistance for $\text{CrAs}_{1-x}\text{Sb}_x$ are presented in figure 2. The measurements were performed during cooling range 300-4K. For $x = 0$, the resistivity curves clearly shows a drop at about 263K followed by a maximum near 230K. For Sb concentrations ($x \sim 0.05$), the maximum becomes more pronounced. The resistance of CrSb exhibits a maxima as the temperature decrease. The drop in the resistance coincides with the antiferromagnetic transition. The transition temperatures are determined from the inflection point in the derivative of the resistivity with respect to temperature. These results are in agreement with transport measurement carried out on single crystal of CrAs by H. Kotegawa *et al* [2]. The antiferromagnetic transition drops to about 150K for $x=0.5$. The variations of the antiferromagnetic transition temperature with Sb concentration is presented in figure 4. The figure shows a sharp linear drop in T_N near $x = 0.45$ with a slope ($\sim -10.67 \text{ K/x}$). This is similar to drop in T_N observed in the variations of T_N with applied pressure reported in [1]. The in antiferromagnetic transition suppressing is striking and is clearly shown in figure 3. It is worth mentioning that superconducting transition in these doped polycrystalline samples have not been observed down to 4.0K, the lowest temperature available in our system.

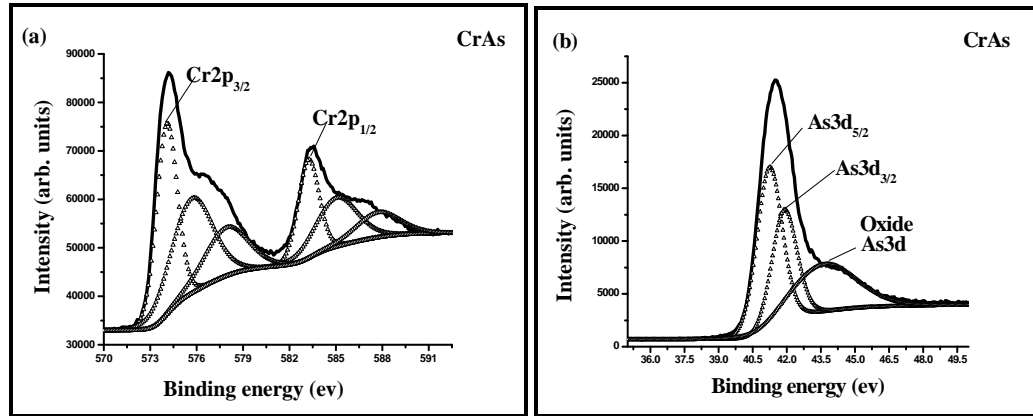


Figure 1: XPS spectra of CrAs sample: (a) Cr2p core level spectrum, (b) As3d core level spectrum. The experimental spectra are represented by solid line. The fitted peaks are represented by open triangle.

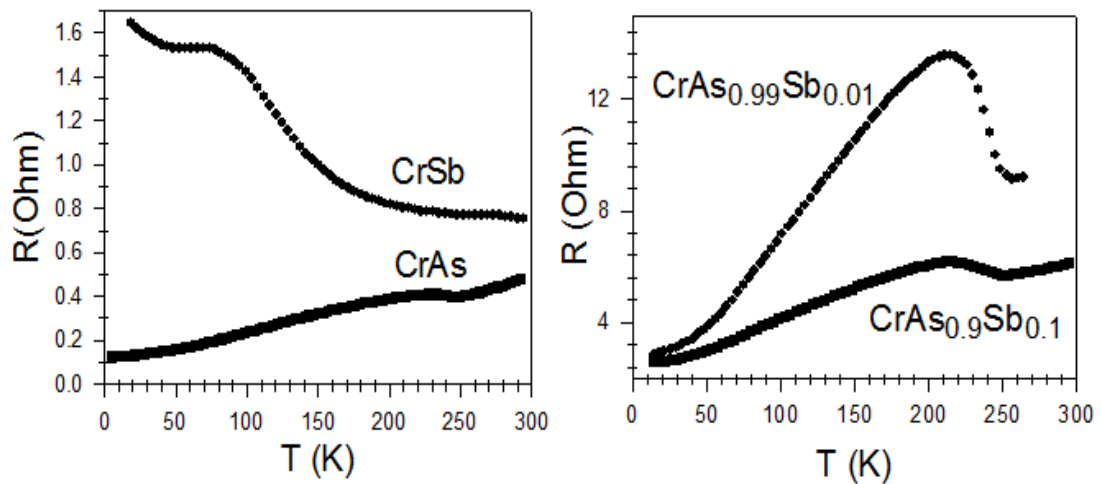


Figure 2: Variations of the resistance with temperature for CrAs_{1-x}Sb_x.

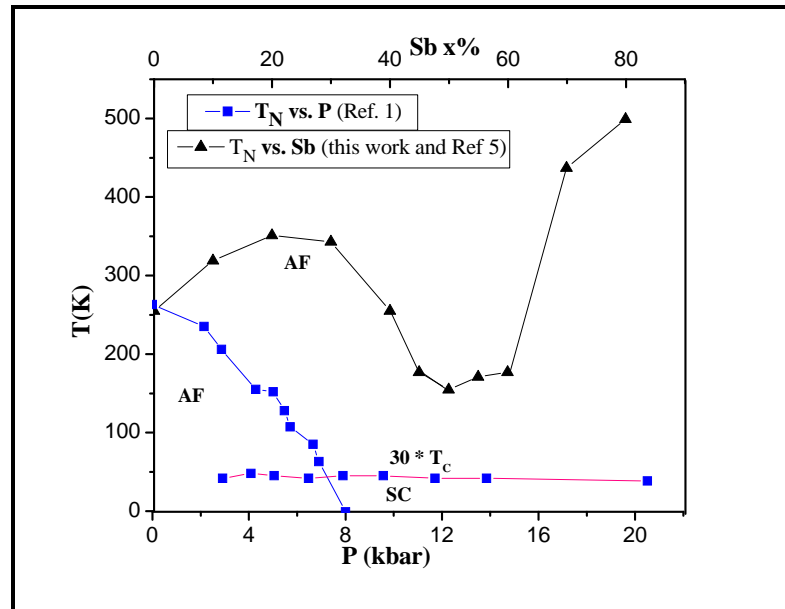


Figure 3: Combined phase diagram of $\text{CrAs}_{1-x}\text{Sb}_x$.

4. Conclusion

XPS analysis revealed that valence states for the elements are Cr^{+3} and As^{+3} did not change with Sb^{+3} substitutions. Transport measurements revealed the antiferromagnetic phase transition that drops with increasing Sb near 0.5, then increase gradually. We observed a liner drop in T_N near $x=0.45$ with linear slope $(-10.7 \frac{\text{K}}{x} \%)$ in a much similar way to the suppression of T_N for CrAs under the effects of external pressure.

Acknowledgments

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