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Thermopower of $Ag_{2+\delta}S$ across the α–β transition*

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Abstract. Thermopower data of $Ag_{2+\delta}S$ in both of its α- and β-phases are reported and the results are compared with the data on $Ag_{2+\delta}Se$.

Keywords. Thermopower; α–β transition; silver chalcogenides.

1. Introduction

Recent Studies (Shukla and Schmalzried 1979; Shukla *et al* 1981) on silver chalcogenides clearly show that the crystallinity and stoichiometry of samples as well as the separation of ionic and electronic contributions to conductivity are important in understanding defect and transport properties of these materials. With single crystals of $Ag_{2+\delta}Se$ of well defined stoichiometry, Shukla *et al* (1981) find that the thermopower does not change markedly across the α-β phase transition reflecting the conducting behaviour of this material; these results differ from those of Junod (1959) who employed polycrystalline samples of ill-defined stoichiometry. Unlike $Ag_{2+\delta}Se$, $Ag_{2+\delta}S$ exhibits a marked change in electronic conductivity at the α-β transition. Thermopower measurements on single crystals of $Ag_{2+\delta}S$ of well defined stoichiometry have not been reported hitherto, the only report being on a polycrystalline sample (Junod 1959). In this paper, we report an *in situ* single crystal study of the thermopower of $Ag_{2+\delta}S$ in both the α- and β- phases at different values of δ.

2. Experimental

Single crystals of silver sulfide were grown in quartz capillaries of 0·8 mm bore by reaction between the elements of very high purity at around 573K. Several tiny Ag/AgI and Pt probes were mounted *in situ* with these crystals. A few thin and fine tiped iron-constantan thermocouples were arranged very near to the crystal for registering its temperature. With this arrangement, the stoichiometry of the specimen could be controlled coulometrically at any temperature. Also, thermopower as well as ionic

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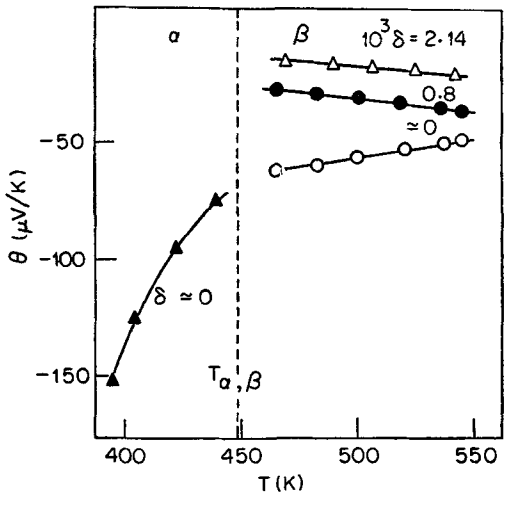
and electronic contributions of conductivity could be measured as a function of δ in both the α- and β-phases (Shukla and Schmalzried 1979; Shukla *et al* 1981).

3. Results and discussion

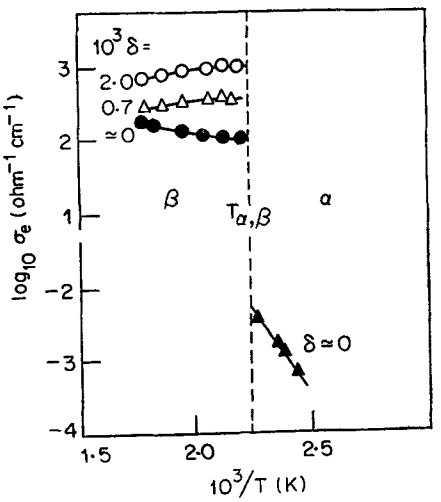
Temperature variation of thermopower for both the phases of $Ag_{2+\delta}S$ are shown in figure 1. We find that the thermopower increases markedly with temperature in the α-phase. In the high temperature β-phase, we find a slight decrease in thermopower with increase in temperature for compositions with $\delta = 2{\cdot}14 \times 10^{-3}$ and $0{\cdot}8 \times 10^{-3}$ while it shows a slight increase with temperature for the nearly stoichiometric compositions ($\delta \simeq \delta^{\circ}$).

We have also measured the electronic and ionic conductivities of Ag_2S in both of its α- and β-phases as a function of δ; the logarithm of the electronic conductivity, $\log_{10} \sigma_e$, is plotted against the inverse of temperature, $10^3/T$, in figure 2. We find from the electronic conductivity data that for the stoichiometric specimen of Ag_2S the activation energy changes from $\sim 0{\cdot}9$ eV to $\sim 0{\cdot}01$ eV across the crystallographic transition. The change in electronic conductivity behaviour (metal to non-metal) of β-$Ag_{2+\delta}S$ phase with δ has been described elsewhere (Shukla and Schmalzried 1979; Shukla *et al* 1981).

Ionic conductivity in both the α- and β-phases of Ag_2S does not change with δ as expected from the thermodynamic considerations (Miyatani 1967). We find a value of 5×10^{-2} ohm^{-1} cm^{-1} and 4·6 ohm^{-1} cm^{-1} for the ionic conductivity in the α- and β-phases of silver sulfide respectively. The ionic conductivity of $Ag_{2+\delta}Se$ is reported to be $10^{-3} - 10^{-4}$ ohm^{-1} cm^{-1} in the α-phase (Ohachi 1974) and ~ 5 ohm^{-1} cm^{-1} in the β-phase (Shukla *et al* 1981). Unlike β-$Ag_{2+\delta}S$, where both the electronic conductivity and the thermopower change from non-metal to metal behaviour as δ approaches



(1)



(2)

Figure 1. Plots of thermopower, θ, against temperature, T, for various stoichiometric compositions of α- and β-silver sulfide.

Figure 2. Plots of electronic conductivity, $\log_{10} \sigma_e$, against inverse of temperature, $10^3/T$, for various stoichiometric compositions of α- and β-silver sulfide.

the stoichiometric value, the thermopower of β-$Ag_{2+\delta}Se$ decreases with increase in temperature, for all the values of δ; the electronic conductivity of β-$Ag_{2+\delta}Se$, however, shows, a change from a metal to non-metal behaviour with the change in δ (Shukla *et al* 1981). The insensitivity of the thermopower of β-$Ag_{2+\delta}Se$ to exhibit the metal to non-metal transition akin to β-$Ag_{2+\delta}S$ may be viewed in light of the following facts: (i) A relatively small change in the magnitude of the electronic conductivity of β-$Ag_{2+\delta}Se$ ($10^{3.6}$ — 10^4 ohm^{-1} cm^{-1}) is found over the entire homogeneity range (Shukla *et al* 1981) as against β-$Ag_{2+\delta}S$ (10^2 — $10^{3.7}$ ohm^{-1} cm^{-1}). (ii) Electronic conductivity of stoichiometric β-Ag_2Se ($\sim 10^{3.5}$ ohm^{-1} cm^{-1}) is approximately an order of magnitude higher than its value for the nearly stoichiometric β-Ag_2S (10^2 ohm^{-1} cm^{-1}) specimen.

The values of activation energies derived from the plots of thermopower against the inverse of temperature for nearly stoichiometric composition of $Ag_{2+\delta}S$ in its α- and β-phases are $\sim 0{\cdot}3$ eV and $\sim 0{\cdot}05$ eV respectively. Although the value of the activation energy for the nearly stoichiometric β-Ag_2S derived from the thermopower data is in the range of the activation energy for a similar specimen obtained from the electronic conductivity data, there is substantial difference between the two values for the α-phase; the activation energy derived from the thermopower data is lower than its value obtained from the conductivity data. This is understandable as the conductivity has the additional mobility activation term. The difference between the two activation energies gives a value of $\sim 0{\cdot}6$ eV for the mobility activation for a nearly stoichiometric α-Ag_2S specimen. Such differences in the conductivity and thermopower data has been observed in oxide materials (Joshi *et al* 1980). The ionic contribution to the thermopower could be neglected in light of the fact that in $Ag_{2+\delta}Se$, where the ionic conductivity across the α-β transformation changes by 3–4 orders of magnitude (Ohachi 1974), hardly any change in the values of the thermopower is seen (Shukla *et al* 1981).

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