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BEHAVIOR OF THE ACTIVATION ENERGY FOR IONIC CONDUCTION IN $RbAg_4I_5$ NEAR 209° K

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ABSTRACT

We have examined the 209°K phase transition of $RbAg_4I_5$ by measuring the differentials of the sample resistance as a function of temperature on single crystals. Our results reveal a continous variation of the activation energy with temperature through the transition which is attributed to the domination of short range order on the ionic conductivity.

RESUMEN

Hemos examinado la transición de fase a 209°K del $RbAg_4I_5$ por medio de la medida de los diferenciales de la resistencia de una muestra monocristalina como función de la temperatura. Nuestros resultados revelan una variación continua de la energía de activación con la temperatura a través de la transición, lo cual se atribuye al predominio del orden de corto alcance en la conductividad iónica.

Very recently, considerable theoretical and experimental effort has been devoted to the problems connected with the phase transitions of crystalline solid electrolytes$^{(1-3)}$. These so-called superionic conductors exhibit states of anomalously high ionic conductivity comparable to those of molten salts or good liquid electrolytes (~ 1 ohm^{-1} cm^{-1}).

Most experimental investigation have been done on the compound $RbAg_4I_5$ which is the solid electrolyte that has the highest ionic conductivity available at room temperature (about 0.2 ohm^{-1}cm^{-1}). This solid undergoes a phase transition at $T_c = 209°K$, which has been characterized by gradual changes in the conductivity and lambda anomalies in the specific heat$^{(4-6)}$.

Here we report the results of precise measurements of the differentials $\Delta R(T)$ of the sample resistance as a function of temperature and through a narrow range centered near $T_c = 209°K$, for single crystals of $RbAg_4I_5$, using the ac - temperature calorimetric method$^{(7)}$. These measurements are shown to give data which support the point that the 209°K phase transition of the considerate solid electrolyte is such that not only its conductivity changes continously but also its activation energy$^{(8)}$.

Since the ac - temperature calorimetry technique is based on the thermodynamic result that under proper conditions when a sample absorbs a certain quantity of heat periodically at a given temperature, the amplitude of the induced temperature oscillation is related to its specific heat, then we used the fact that this ac modulation of the sample temperature introduces modulations on other sample properties to measure $\Delta R(T)^{(9)}$.

Wafers of single crystals of approximately 10 mm^2 were thinned to about 0.1 mm using dry abrasive. These samples were wired for four probe electrical measurements using a 50-μm gold wire attached with silver paint dissolved in toluene. The samples were electrically excited by applying a constant sine wave current ($I_o = 50\mu A$, $W_1 = 10$ kHz). The electrical resistance of the samples were modulated by the temperature oscillations induced in them by a square power input of frequency

$W_\circ \simeq 1.5$Hz, produced by a beam of light chopped at this frequency. The corresponding amplitudes of the induced voltages oscillations with sidebands at frequencies $W_1 \pm W_\circ$, that is, $\Delta V = \Delta R \cdot I_\circ$, were detected by first demodulating the resulting amplitude modulation of the ac - voltage from the carrier and then using a lock-in amplifier referred to the phase and frequency $W_\circ$ of the chopped light. These amplitudes ΔV were of the order of 10 - 100 nV, such that $\Delta R/R$ were of the order of 10^{-7} - 10^{-6} near T_c.

A typical result of ΔR for the sample resistance on single crystals of $RbAg_4I_5$ as a function of temperature and for a range close to the 209°K phase transition is shown in Fig. 1. Assuming an Arrhenius relation for the conductivity in the critical region, $\sigma = \sigma_\circ \cdot \exp(-E(T)/k_BT)$, so that the sample resistance is given by $R = R_\circ \cdot \exp(E(T)/k_BT)$, then

$$\frac{\Delta R}{R} = \Delta \left(\frac{E}{k_BT} \right) \tag{1}$$

and so, a continous variation of ΔR through $T = T_c$, as Fig. 1 shows, implies that ΔE is also continous across the transition. This is contrary to previous results$^{(10,11)}$, which indicate that an Arrhenius plot of ℓnR vs. $1/T$ show a sudden change of slope across the transition, from a constant value E_1 of the activation energy below T_c to another constant value E_2 above T_c; the first value being a little higher than the second one.

It is worth mentioning that, far from T_c, our results agree quite well with previous determination of the activation energy: notice from Fig. 1 that out of the critical region $\Delta E = 0$, and that ΔR behaves like $(-E/k_BT^2)$. Moreover, since in the ac - calorimetry method $\Delta T \propto 1/c_p$, where c_p is the specific heat of the sample and which is almost constant for $RbAg_4I_5$ out of the critical region, then our results also show that $E_1 > E_2$.

The experimental fact that the activation energy $E(T)$ is higher below T_c and the continous change from the lower value above T_c takes place in a relatively narrow region of temperature (of about 1°K), indicates that some kind of local order is gradually stablished when the crys-

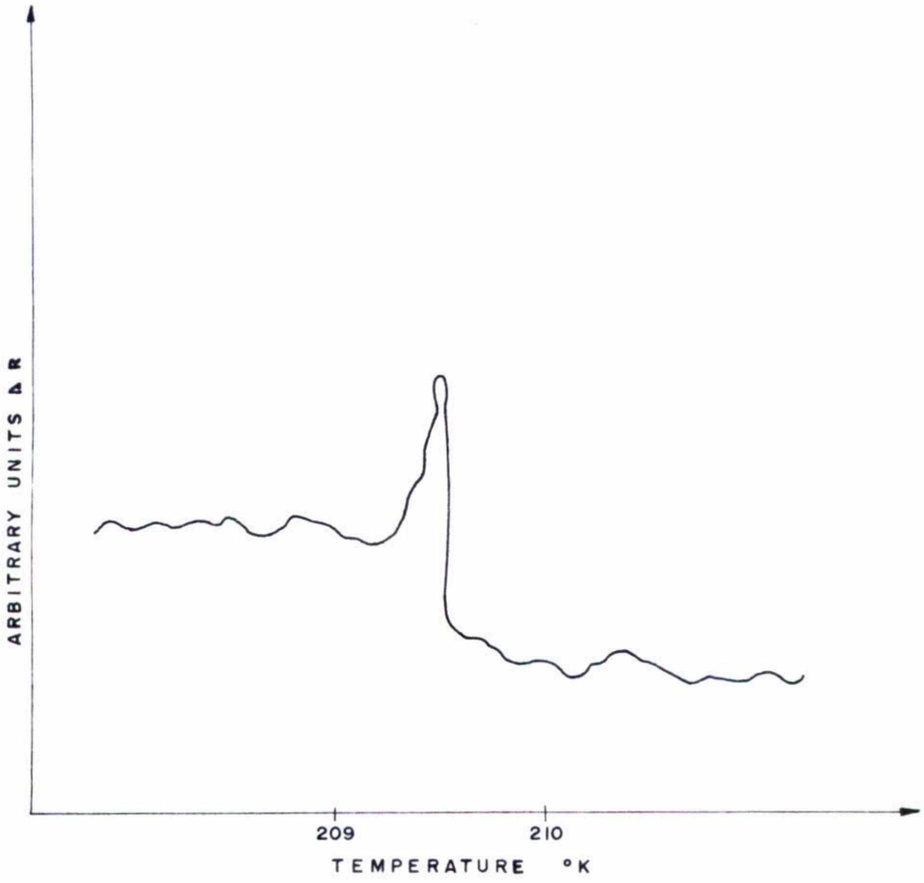

Fig. 1 Sample resistance differentials of $RbAg_4I_5$ vs. temperature in the vicinity of the 209°K phase transition.

tal goes below T_c due to nearest-neighbor correlation effects on the diffusion species. This is also an explanation of the accompanied singular behavior of the specific heat in this critical region due to the rapid decrease in entropy, $(\partial S/\partial T)_P = C_P/T$.

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