

HIGH RESOLUTION AC CALORIMETER FOR SOLID ELECTROLYTES

ELECTROLYTES

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ABSTRACT

The ac temperature technique is used to develop a calorimeter for measuring heat capacities and activation energies for ionic conduction in solid electrolytes. It can measure these properties changes of 1 part in 10^3 with a temperature resolution better than 10 mK from 4°K to 380°K in the neighborhood of a phase transition. This calorimeter has used to study the 209°K phase transition of RbAg_4I_5 .

RESUMEN

La técnica de temperatura ac es usada para desarrollar un calorímetro que mida capacidades caloríficas y energías de activación de conducción iónica en electrolitos sólidos. Puede medir cambios de estas propiedades dentro de una parte en 10^3 con una resolución en temperatura mejor que 10 mK desde 4°K hasta 380°K en la vecindad de una transición de fase. Este calorímetro ha sido usado para estudiar la transición de fase a 209°K de RbAg_4I_5 .

1. INTRODUCTION

Over the past few years intensive theoretical and experimental efforts have been devoted to the study of phase transitions and critical phenomena^(1,2). These efforts have been largely enhanced by the success of scaling hypothesis and its renormalization approach in solving many of the problems and in making important predictions for certain classes of materials which have been lately confirmed by the experiments⁽³⁾. One of such system that has received considerable attention is that of solid electrolytes or superionic conductors which possess properties that are common to both solids and liquids^(4,5).

In order to compare the theoretical results with the experimental ones the property measurements should be made arbitrarily close to the point transformation, T_c , where thermal noise becomes most of the time very large and so, the time required to approach thermal equilibrium after a disturbance, is very long. This in fact makes experimental work difficult. It is, therefore, required very high temperature resolution and, at the same time, extreme sensitivity to small changes in the measured property. When the samples are so small as the single crystals of solid electrolytes which we are able to grow or when the thermal conductivity of the samples are very low as most of these materials, using the traditional adiabatic techniques to measure their heat capacities or ionic conductivities is hard to have the necessary resolution or sensitivity.

Since the ac heat capacity method has become a very powerful technique for measuring thermal properties of solid samples under the existence of thermal leak to a bath reservoir rather than under adiabatic conditions^(6,7), we have developed an apparatus in which the samples are heated by radiation and utilizes this ac-temperature approach to make high resolution measurements on superionic conductors.

2. PRINCIPLES AND APPARATUS

A small sample chamber -longer dimension 5 cm- is filled with a thermal exchange gas as shown in Fig. 1. The base of the chamber is a

thick copper cylinder, which acts as heat sink. A wafer of single crystal of approximately 8 mm^2 in area and about 0.1 mm thickness is suspended in the medium very close to the heat sink by fine Chromel-Alumel thermocouple wire, $25 \mu\text{m}$ diameter, fixed on the rear surface of the sample with minute amounts of silicone grease. An ac-modulated light beam irradiates the upper surface of the sample, which is coated by a thin layer of graphite in order to maximize light absorption: this provides an oscillating heat input to the sample. Its thermal response is detected with the thermocouple.

Considering a one-dimensional heat flow process through the sample and the exchange gas to the thermal bath⁽⁷⁾, the resulting temperature oscillation of the rear surface of the sample (at $x=d$) can be expressed in the form

$$T(d,t) = T_0 + T_{dc} + T_{ac} e^{i(\omega_0 t - \phi)} \quad , \quad (1a)$$

when the power input to the upper surface (at $x=0$) of the sample is $P(t) = P_0 + P_1 e^{i\omega_0 t} + \dots$, and where

$$T_{dc} = P_0 L / K_g \quad , \quad (1b)$$

$$T_{ac} = \frac{1}{(1 + 1/\omega_0^2 \tau_{rs}^2 + \omega_0^2 \tau_s^2)^{1/2}} \frac{P_1}{\omega_0 \rho_s d C_s} \quad , \quad (1c)$$

$$\phi = \sin^{-1} |1 + (1/\omega_0 \tau_{rs} + \omega_0 \tau_s)^2|^{-1/2} \quad . \quad (1d)$$

Here T_0 is the thermal bath temperature, d is the thickness of the sample, L is the distance from the sample to the thermal bath, C_s is the heat capacity per gram of the sample, ρ_s is the mass density, K_g is the thermal conductivity of the exchange gas, τ_s is the thermal relaxation time of the sample (defined by $\tau_s = d^2/k_x$, where k_x is its thermal diffusivity) and τ_{rs} is the sample-reservoir relaxation time associated with the thermal interaction between the two systems through the ex-

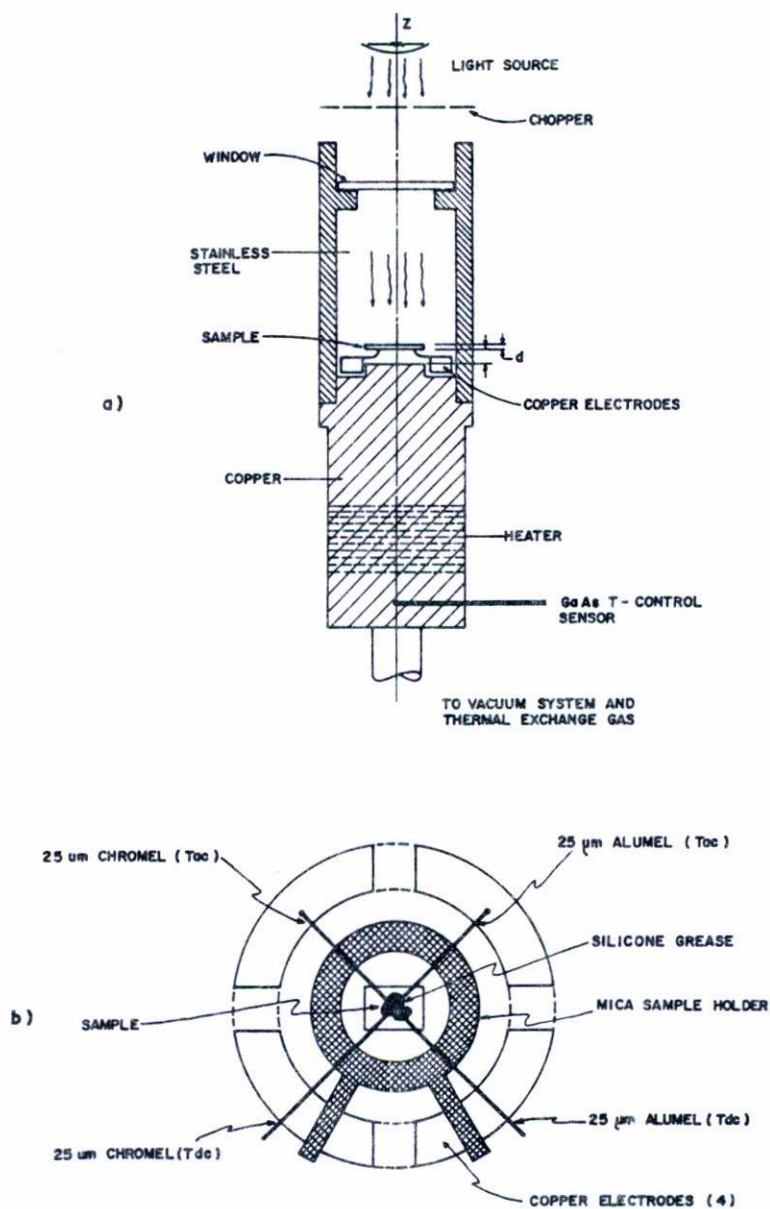


Fig. 1 Temperature modulation calorimeter: (a) schematic views of the sample chamber and (b) of the sample holder.

change gas (defined by $\tau_{rs} = C_s \rho_s L d / K_g$).

If the calorimeter is operated at an ω_0 such that

$$\tau_{rs} \gg 1/\omega_0 \gg \tau_s \quad . \quad (2)$$

Then, the time varying part of Eqs. (1), T_{ac} , can be simplified and solved for the heat capacity of the sample, obtaining

$$C_s = \frac{P_1}{\omega_0 \rho_s d} \left(\frac{1}{T_{ac}} \right) \quad , \quad (3)$$

which is the basic equation of the ac-calorimetry. The amplitude T_{ac} was detected with a lock-in amplifier referred to the phase and frequency ω_0 of the chopped light. Because the measured signal, T_{ac} , is repetitive, signal averaging technique as the phase-coherent-ac-detection can be used to minimize the effect of noise. As a result, heat capacity changes as small as 0.1% of the total can be detected. Also, since the amplitude of the temperature oscillations is small (typically $T_{ac} \lesssim 1\text{mK}$), mainly near a phase transition, the resolution is inherently good.

The small ac-temperature modulation induced in the sample on the top of the dc "bias" equilibrium temperature of the system (sample-exchange gas- heat reservoir) can introduce modulation in the response of the sample to other macroscopic fields applied to it⁽⁸⁾. We used this fact to measure

$$\Delta R(T) \approx \left. \frac{dR}{dT} \right|_{T_{dc}} T_{ac} \quad , \quad (4)$$

for the sample resistivity (here $T_{dc}' = T_0 + T_{dc}$) when it is electrically excited by a constant sine wave current ($I_0 = 50 \mu\text{A}$, $w = 10 \text{kHz}$) and its response detected by first filtering and demodulating the ac-voltage signals, and then using the narrow band detection of a lock-in amplifier with reference frequency ω_0 to get $V = \left(\left. \frac{dR}{dT} \right|_{T_{dc}} T_{ac} \right) I_0$, as we will de-

scribe it in Sec. 3.

3. EXPERIMENTAL MEASUREMENTS

To examine the present method, representative samples of solid electrolyte RbAg_4I_5 were used (this material undergoes a second order phase transition near 209°K ⁽⁹⁻¹¹⁾). The thermal link between the sample and the heat reservoir was provided by 1-10 torr of argon gas. Chopped light of carefully controlled frequency, w_0 , and intensity was used to induce the temperature oscillations in the sample. The measurements were performed in a liquid helium cryostat depicted in Fig. 2.

Estimated values for the relaxation times defined above were made for the appropriate dimensions and the known physical parameters of AgI , which are of the order of $\tau_{\text{int}} = 10 \text{ s}$ and $\tau_s = 10^{-3} \text{ s}$. Measurements of T_{ac} versus w_0 in the range $0.5 \text{ Hz} < w_0 < 10 \text{ Hz}$ confirm the inverse relationship of Eq. (3). The optimum operational chopped frequency was approximately 1.5 Hz.

The experimental setup for measuring T_{ac} and $\Delta R(T)$ of the sample is schematically shown in Fig. 3 which shows the optical system for collimating the light falling on the front face of the sample and the electronic apparatus for detecting the amplitude of the temperature oscillations of the sample, T_{ac} , its average dc-temperature, T_{dc} , and the differentials of the sample's resistance, $\Delta R(T)$ (notice that T_{ac} and ΔR are not measured simultaneously and the corresponding electronic apparatus for each measurements is shown in the same figure for reason of clarity).

The heat capacity measurements are obtained by making a continuous record of the amplitude of the induce temperature oscillations of the sample, T_{ac} , while slowly sweeping the mean temperature of the sample (the temperature controlled unit of the sample's chamber is not shown in Fig. 3). A typical sweep period was of the order of 1 K/h. The output of the lock-in amplifier (corresponding to T_{ac}) and the micro-volmeter (nule detector of the potentiometer for measuring the dc-temperature signals of the sample) were recorded on a two channel strip chart

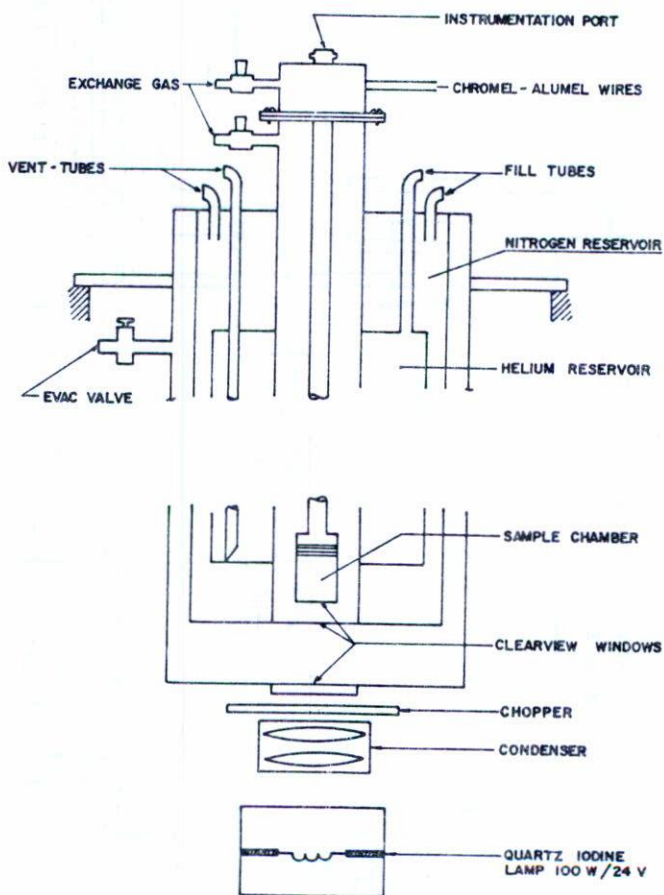


Fig. 2 Detailed view of the liquid helium optical cryostat, probe and light system.

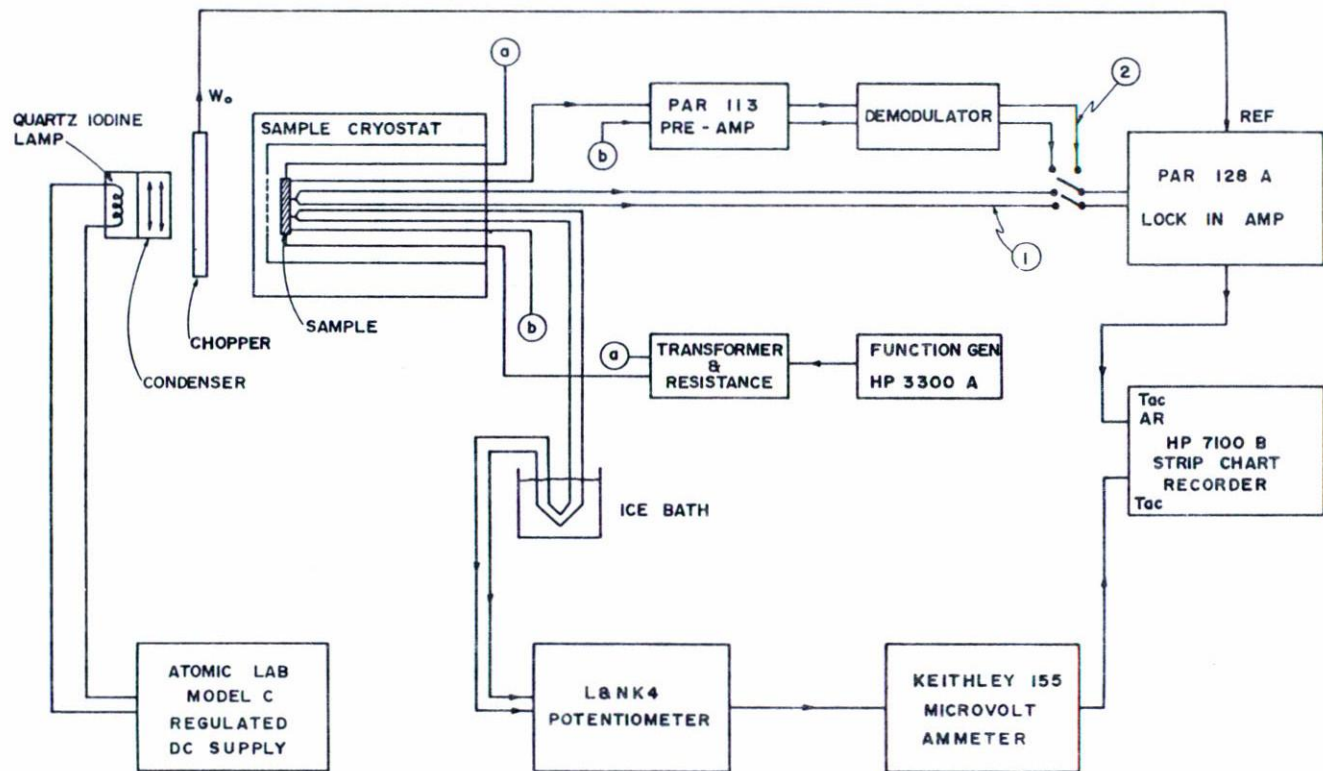


Fig. 3 A schematic diagram of the experimental setup for measuring the specific heat and the differentials of the samples resistance as a function of temperature. Leads (1) are for temperature oscillations and leads (2) for the resistivity measurements. The temperature control system is not shown.

recorder. Data were transferred from the chart record to computer cards. A simple program converts the data points to heat capacity versus temperature.

The ac-technique of measuring the specific heat does not give its absolute value, when, by experimental convenience to avoid physical coupling to the sample, the heat flux to the sample is applied by means of mechanically chopped light, so the relation between ΔT and C_p , according to Eq. (3) was taken equal to 1, and therefore, the C_p data points are given in arbitrary units.

The differentials of the sample resistance, ΔR , were measured by the four-terminal method. Since only ac electrical signals of very low current density should be applied to the samples to reduce polarization effects and plating out of the anode⁽¹¹⁾, one must be careful to avoid offset voltage drift into the samples. The ac-constant current was produced by connecting a 100 k Ω standard resistance in series with the sample in the secondary of an isolation transformer whose primary was driven by a high purity sinusoidal voltage controlled generator. The resulting ac voltage signals across the samples, modulated by the induced temperature oscillation of amplitude T_{ac} and frequency $\omega_0 = 1.5$ Hz, were fed into a low-noise preamplifier to bring the signal to a level sufficiently high to overcome pickup and to drive the demodulator. The filtered output of the demodulator went into the input of the preamp stage of a lock-in amplifier referred to the phase and frequency ω_0 of the chopped light. These amplitudes ΔV were of the order of 10-100nV, such that $\Delta R/R$ were of the order of 10^{-7} - 10^{-6} near T_c .

The first measurements with this apparatus were near the 209°K phase transition of the solid electrolyte $RbAg_4I_5$. Typical plots of the temperature dependence of the heat capacity, C_p , and the differentials of the resistance, ΔR , are shown in Figs. 4, 5, respectively, for a single crystal sample of $RbAg_4I_5$ grown from solution⁽¹²⁾. A preliminary discussion of the ΔR measurements carried out on this compound have appeared elsewhere⁽¹³⁾. As is seen from the Fig. 4 for C_p versus T plot exhibits the λ type anomaly as previous results are shown⁽⁹⁻¹¹⁾ and no latent heat was detected.

In summary, we have developed an apparatus that can resolve a

part in 10^3 change in heat capacity and differential of the sample resistance ΔR (which is related to the activation energy for ionic conduction⁽¹³⁾) with a temperature resolution of 1 mK. Sample size ranges in 0.1 mm by 3 mm^2 or about $100 \text{ }\mu\text{g}$ of solid electrolyte. A drawback of the design described here is the difficulty in knowing precisely the relation between T_{ac} and C_p (Eq. (3)) and therefore, it does not give its absolute value.

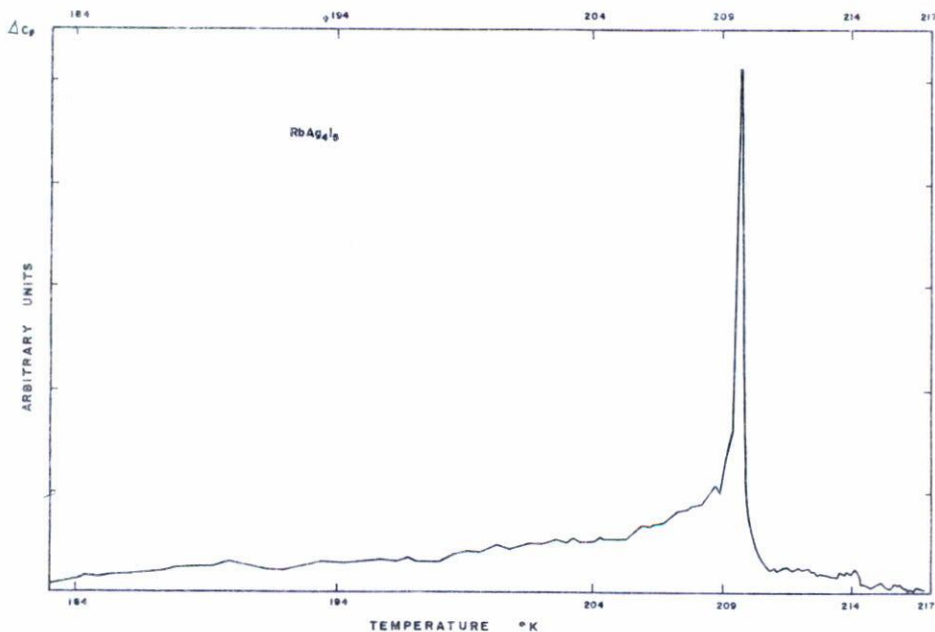


Fig. 4 Specific heat of RbAg_4I_5 versus temperature near its 209°K phase transition.

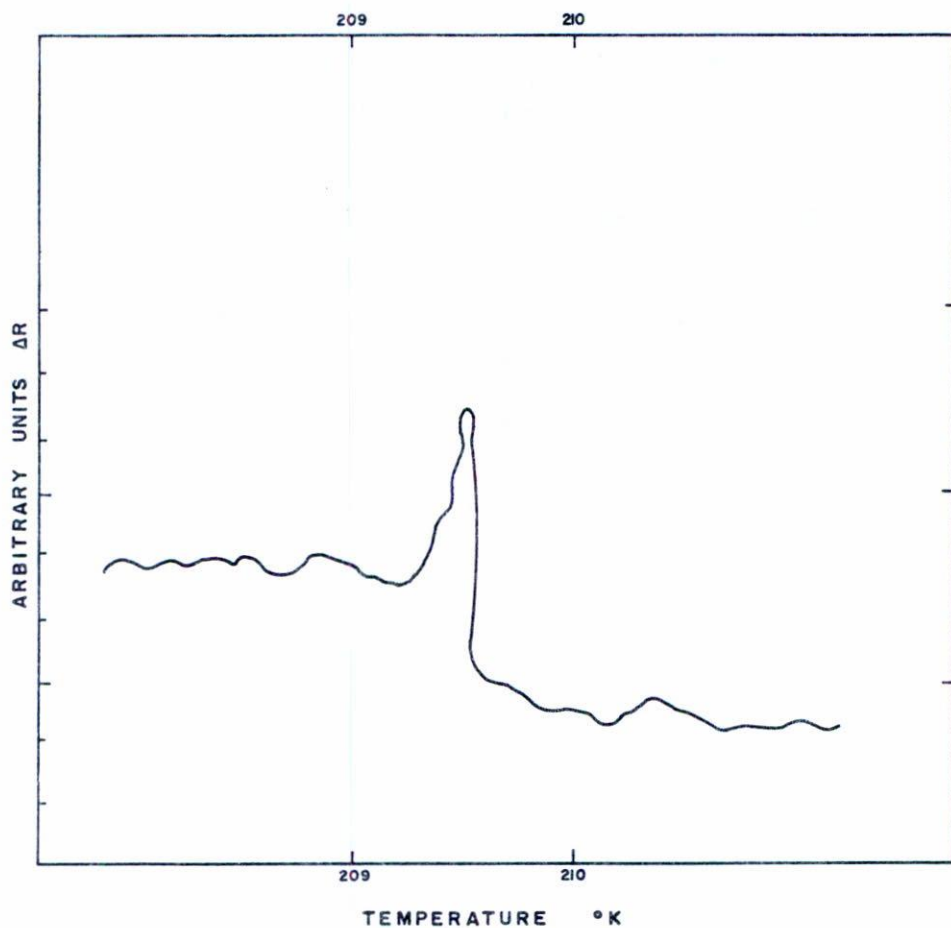


Fig. 5 Sample resistance differentials of RbAg_4I_5 versus temperature in the vicinity of the 209°K phase transition.

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