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Thermal characterization of materials at high pressures

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This review deals with the development of some novel techniques for the measurement of thermal properties of materials at ambient and high pressures. Thermal characterization techniques like Absolute thermoelectric—power, AC electrical Resistivity, Differential thermal analysis and AC Calorimetry with specific reference to their usage at high pressures will be discussed in some detail. Some typical data on materials like Chromium alloys, Chalcogenide and metallic glasses will be presented.

1. Introduction

Thermal characterization techniques center around the measurement of a physical property of a sample subjected to a programmed rate of heating/cooling. Differential thermal analysis (DTA), Differential scanning calorimetry (DSC), Thermo gravimetric analyzer (TGA) are the well known group of techniques widely employed to study physical or chemical changes in materials induced by temperature. However measurement of such properties as electrical resistivity (ρ), Absolute thermoelectric power (TEP) and AC Specific heat (C_P) on metallic samples subjected to a linear rate of heating/cooling can provide valuable information on the electronic band structure and this group of techniques also come under the broad classification of thermal analysis. In what follows, we describe the instrumentation developed by us on thermophysical techniques such as Differential Thermal Analyser (DTA), Electro thermal analyzer (ETA), Thermopower Analyser (TEPA) and AC Calorimeter (ACCAL). However the adaptability of these systems to high pressure environment requires special designing of the sample holders. These aspects along with some typical experimental results on Chromium based alloys, Chalcogenide glasses and Metallic glasses will be discussed.

2. Differential thermal analyser

DTA is a technique to record a thermal event in the sample by comparing it with a reference material, which is devoid of any physical or chemical changes in the temperature range of interest. The DTA cell is machined out of pyrophyllite with symmetrical bores to contain the sample and a reference material like alumina. Chromel-Alumel thermocouples are in direct contact with the sample and reference and are brought out of the high-pressure assembly through four-hole ceramic tubing. The thermocouple signal from the reference chamber is used in the programmed heating of the cell assembly. The differential signal between the sample and the reference, ΔT, is amplified in a Keithley nano-volt amplifier. The input from the Chromel-Alumel thermocouple in thermal contact with the reference material (Alumina) is routed through a differential input filter followed by a high quality amplifier with automatic cold junction compensation and digitized using a high quality 16 bit A/D converter. The digitized thermo-emf signal is then linearised using a polynomial curve fitting software to read the temperature directly. A propriety PID algorithm coupled with a 16 bit D/A converter and a power amplifier provides the necessary power to the heating element, which in the present case is a nichrome heating element. The teflon cell and the high temperature high pressure cell arrangement for a variety of thermo-physical measurements have been discussed in detail elsewhere [1–3]. Temperature stability $\approx \pm 0.02°$C has been achieved. If the set point value in the PID algorithm is incremented linearly with time, the temperature of the sample will follow suit provided the heating rate selected is slower than the rate of control action. Linear rate of heating/cooling, which is software selectable in the range 1 to 20°C per minute, has been achieved in the present setup. It is worth mentioning that to achieve this linear rate of heating, sufficient care has to be taken in positioning the sample holder inside the furnace. Real time digital signal filtering has been employed for improved signal to noise ratio. The software has also

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a provision for real time plotting of the DTA signal (ΔT) as a function of temperature.

2.1. DTA studies on chalcogenide glasses

In the literature, the phenomenon of glass transition has been extensively studied as a function of composition in multi component systems. The effect of pressure on the glass transition has received less attention. The thermodynamics aspects of the glass transition and effect of pressure on Tg have been discussed in detail by Goldstein [4]. In their classic paper, Davies and Jones [5] derived an expression for the pressure coefficient of Tg based on the hypothesis that the glass transition, although kinetically driven occurs when some internal order parameter characterizing the thermodynamic state reaches a critical value. This relation is essentially the Ehrenfest relation for a second order phase transition viz.,

$$\frac{dT_g}{dP} = T_g V_g \frac{\Delta\alpha_P}{\Delta C_P}$$

Where $\Delta\alpha_p$ and ΔC_p are the discontinuities in the thermal expansion and specific heat at the glass transition respectively. It is implicit here that the entropy difference between the two phases is constant at T_g. On the other hand, if the difference in the molar volume between the two phases, ΔV is constant, then we have

$$\frac{dT_g}{dP} = \frac{\Delta K_P}{\Delta\alpha_P}$$

where, ΔK_T and $\Delta\alpha_P$ are discontinuities in the isothermal compressibility and volume expansion at the phase transition. Experimental determination of dT_g/dP is thus important to validate either the "iso-entropic model" or the "iso- free volume model". Using DTA as a diagnostic tool the pressure effect on T_g for a standard switching glass $As_{40}Se_{30}Te_{30}$ has been studied [6].

Fig. 1 gives the DTA curve for the chalcogenide glass $As_{40}Se_{30}Te_{30}$ at ambient pressure. The details of the sample preparation is described elsewhere [6]. A heating rate of 10°C/minute was employed for these measurements. The sample was heated to a temperature beyond T_g at this rate and cooled at the same rate. The data presented in the Fig. 1 corresponds to the second cycle of heating at the same rate. Normally glass transition manifests as a shift in base line due to heat capacity changes near T_g. The value of T_g determined from this curve is around 135°C and agrees well with the one determined from the standard DSC apparatus. The thermogram at 21 kbar is given in Fig. 2. The error in measurement of ΔT is ± 0.05°C and error in the temperature measurement is ± 0.5°C. These experimental data were collected after the sample was pressurized in the glassy phase at a temperature much below T_g and subjected to a heating and cooling cycle at the same rate. It is clear that the T_g has shifted to higher temperatures with the application of pressure. We also note that the base line becomes steeper at higher pressures due to the mismatch in the heat capacities of the sample and reference at higher pressures. However the anomaly near T_g is still pronounced and the transition could be tracked up to 20 kbar. Different heating rates were used to carry out the high pressure DTA experiments (5°C/min and 10°C/min). All the scan rates lead essentially to the same value of $dT_g/\mathrm{dP} \approx 9°\mathrm{C/kbar}$.

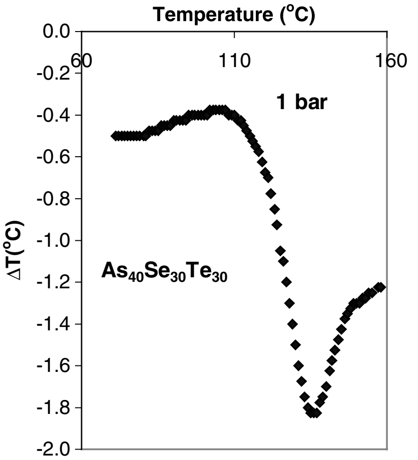

Figure 1 DTA curve for chalcogenide glass at ambient pressure.

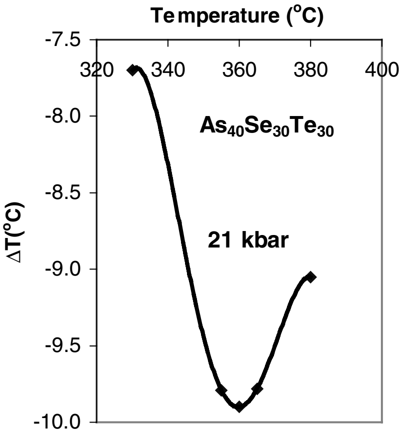

Figure 2 Thermogram at 21 kbar.

3. Electro thermal analyzer (ETA)

The measurement of electrical resistivity of metallic samples, semiconductors etc. as a function of temperature is of importance both from the view of basic and applied research. The system developed by the authors is based on the well-known four-probe technique for resistivity measurement. The standard four probe method of measuring resistivity as a function of temperature at high pressures generally requires six leads to be brought out of the high pressure cell of diameter less than 12 mm. Conventional Piston—Cylinder apparatus was used for generation of high pressures up to 40 kbars. For truly hydrostatic measurements up to 250°C the teflon cell technique [7] is employed and for higher temperatures up to 1000°C the quasi hydrostatic technique is employed [8]. Bringing out this many leads poses some experimental difficulties. The authors have developed a novel technique [9] for AC resistivity measurement where only four leads are taken out from the high-pressure cell. Pressure has been calibrated using standard 'fixed point' method resulting from polymorphic phase transitions in well-known metals. In the pressure range 0-40 kbar the Bismuth I–II and II–III transitions were utilized to calibrate the ram pressure against the true pressure seen by the specimen.

The two pairs of thermocouples spot welded to the sample at either ends are used for passing the AC current (across *Chromel–Sample–Chromel*), measuring the AC voltage developed across the sample (*Alumel–Sample–Alumel*), and also for measuring the temperature (DC *voltage developed across the thermocouples*). It would suffice here to mention that the magnitude of the current could be varied continuously from 0 to 50 mA and the high output impedance (≈ several MΩ) ensures that the current through the metallic sample is constant irrespective of its impedance. The AC voltage developed across the sample that is proportional to the sample resistance is measured with a DSP Lock-in-Amplifier (Stanford Research Systems, Model SR 830). The output voltage from the Lock-in-amplifier is accessed directly to the PC through its IEEE 488 interface. Simultaneous measurement of temperature is achieved by measuring the DC component of the differential voltage developed across the current and the voltage leads, which are in close proximity. A low pass active filter essentially removes the AC component and the DC output forms the input to the temperature lineariser and controller/programmer. It is thus possible to carry out high resolution AC resistivity studies either in the isobaric or isothermal mode of measurement. In this set up it is possible to detect changes in resistivity ≈1 part in 1000.

3.1. Pressure studies on the magnetic transitions in chromium based alloys

Chromium alloy systems exhibit a rich variety of magnetic transitions and have been studied extensively at ambient pressure and also at high pressures [10]. It is well established that these magnetic transitions are associated with the nesting of the Fermi surface. Pure chromium is an itinerant antiferromagnet described as an incommensurate spin density wave below the Neel temperature (311°K). This unique type of antiferromagnetic ordering is due to the attractive Coulomb interaction between electron and hole pockets near the Fermi surface, which have approximately the same octahedral shape and size. This interaction leads to an energy gap right at the Fermi surface and gives rise to well defined anomalies in electrical resistivity and TEP. Alloying studies have established that there is a correlation between the electron to atom ratio (e/a) and the Neel temperature (T_N) and also the type of antiferromagnetic ordering. For alloying with elements whose e/a < 6, it has been experimentally observed that the magnitude of T_N is lowered and the spin density wave remains incommensurate with the lattice. On the other hand, alloying with elements whose e/a $>$ 6 leads to a rapid increase in T_N and importantly the nature of the spin density wave changes to a commensurate type at a critical concentration. The effect of pressure on different magnetic transitions like the commensurate-paramagnetic (C-P), incommensurate-paramagnetic (I-P), and incommensurate-commensurate (I-C) phases in Chromium based alloys are of fundamental interest. The magnetic phase diagram in the pressure—temperature plane is remarkably similar to that in the composition—temperature plane in these systems. This observation has led to the general view that increasing pressure is equivalent to alloying Chromium with an element whose e/a < 6. Extensive work has been carried out by the authors on several alloy systems like $Cr_{0.99}Rh_{0.01}$, $Cr_{0.995}Rh_{0.005}$, $Cr_{0.95}Mn_{0.05}$, $Cr_{0.99}Re_{0.01}$ and $Cr_{0.995}Re_{0.005}$ where electrical resistivity is employed as a diagnostic tool to delineate C-P, I-P and C-I magnetic phase boundaries [11–13].

Fig. 3 gives the plot of resistance versus temperature at different pressures up to 6 kbar in a typical Chromium-Rhodium alloy. The resistivity anomaly near T_N manifests as a weak minimum for this alloy system.

The anomaly near 175°C at 1 kbar is thus associated with the commensurate-paramagnetic (C-P) phase transition. The error in measurement of temperature is 0.5°C and error in resistance measurement is ±0.02 mΩ.

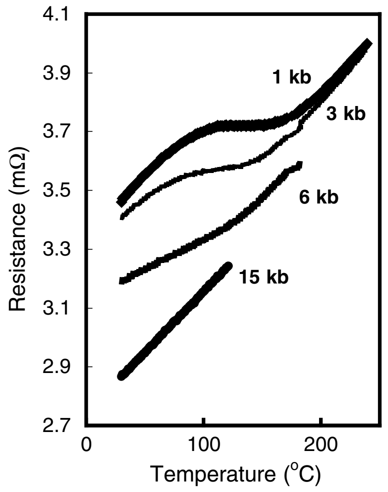

Figure 3 Resistance variation with temperature in $Cr_{.995}Rh_{.005}$ alloy.

Pressure has a marked effect on the nature of the resistivity anomaly accompanied by a strong depression in the magnitude of T_N. It may be noted that at a pressure of 6 kbar, the C-P transition manifests as a change of slope near 120°C. We note that the characteristic resistivity anomaly almost vanishes in the region beyond 12 kbar and it is impossible to track this phase boundary at higher pressures.

4. Thermopower Analyser

TEP is perhaps the most sensitive among the electronic transport properties in metallic systems. It is well known that TEP is related to the energy derivative of the density of states and the relaxation time of the conduction electrons evaluated at the Fermi energy. TEP has not been used extensively to study the electronic structure of materials in comparison with the conventional resistivity technique. This is mainly due to experimental problems associated with the measurement of TEP in an automated way. In this direction we have developed several techniques for automatic measurement of this property under controlled conditions of temperature and pressure [3, 14, 15].

Fig. 4 gives a typical TEP data on the same Cr-Rh alloy where distinct anomalies are observed even beyond 12 kbar. The error in measurement of temperature is ±0.5°C and error in TEP measurement is $\pm 0.02 \mu V/°C$. TEP technique thus provides a powerful diagnostic tool to study subtle phase transitions driven either by temperature or pressure.

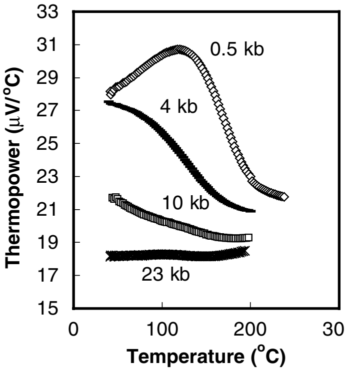

Figure 4 TEP versus Temperature for $Cr_{.995}Rh_{.005}$ alloy.

5. AC Calorimetry (ACCAL)

The basic principle involved in ac calorimetry is to measure the linear response of the sample subjected to oscillatory heat input. The temperature rise in the sample consists of an oscillatory part and a dc part. In what follows we consider the simple case of a metallic sample where the oscillatory heat input is provided by passing a current through it. It is clear that if the current through the sample is at frequency, ω, the oscillatory part of the temperature rise is at frequency, 2ω. The amplitude of the oscillatory part, ΔT_{ac}, is inversely related to the specific heat, C_P, through the relation

$$C_P = \frac{I_0^2 R}{m\pi\omega\Delta T_{ac}}, \quad \omega > \omega_{\text{relaxation}}$$

Here I_0 is the amplitude of the current , R the resistance of the sample, m the mass of the sample under study. $\omega_{\text{relaxation}}$ is the relaxation frequency, which describes the rate of heat transfer to the surrounding pressure transmitting medium and is given by the expression.

$$\omega_{\text{relaxation}} = \frac{K}{C_p}$$

where K is the thermal conductivity of the pressure transmitting medium. It turns out that choosing low thermal conductivity pressure transmitters like silicone fluid, talc etc., the relaxation frequency turns out to be in the range of 0.3 to 2 Hz. The operating frequency should thus be higher than the relaxation frequency and yet sufficiently low so that the sample maintained internal thermal equilibrium during heating cycle. This technique suitable for ambient and high pressure has been explained in detail in reference [16]. It may be noted that the resistance of the sample can change either due to pressure or temperature. Simultaneous measurement of resistance of the sample is a prerequisite for ac specific heat measurements. This aspect has been taken care of in this technique. The amplitude of the temperature oscillation is measured accurately using a DSP Lock-in amplifier.

Samples of low mass metallic glass in thin ribbon form were used in the present high-pressure investigation. A 40SWG chromel-alumel thermocouple was spot welded to the center of the specimen and is used as a probe to measure the oscillatory part of the temperature signal and also the mean temperature of the sample. The resistivity of the sample is simultaneously measured using the four-probe technique using a digital multimeter operated for low frequency RMS detection. Dedicated software developed for the IEEE 488.2 bus facilitates data acquisition, programmed rate of heating and real time plotting of the resistivity and specific heat data as a function of temperature. Talc was used as a pressure-transmitting medium and high pressure experiments were carried out in a conventional Piston-cylinder apparatus.

Fig. 5 presents some new results on the pressure effect on the curie temperature in an amorphous ferromagnetic metallic system like the metallic glass $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$.[17]. The error in measurement of temperature is ± 0.5°C and error in ΔT measurement is ± 0.002°C. Unlike the case of the crystalline ferromagnet like Nickel or Iron, pressure has a marked effect on the

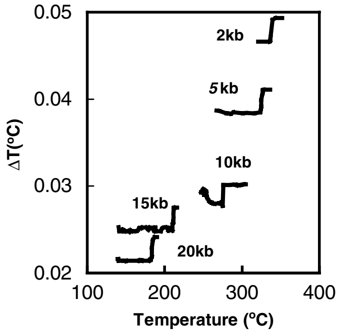

Figure 5 ΔT_{ac} vs temperature at different pressures in metallic glass $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$.

Curie temperature in this metallic glass. dT_C/dP is negative and its magnitude increases dramatically at higher pressures. This behaviour is characteristic of the Invar alloys with low thermal expansion coefficient.

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