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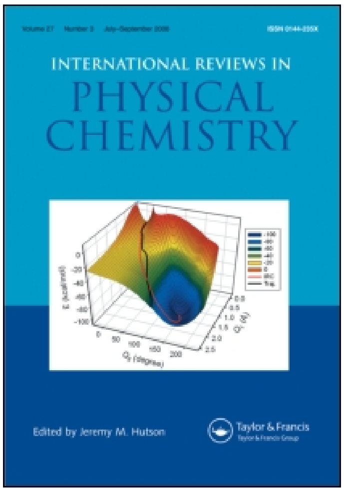

International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Recent Applications of Heat Capacity Measurement in Physicochemical Investigations

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To cite this Article Lakshmikumar, S. T. and Gopal, E. S. R.(1982) 'Recent Applications of Heat Capacity Measurement in Physicochemical Investigations', International Reviews in Physical Chemistry, 2: 3, 197 — 235

To link to this Article: DOI: 10.1080/01442358209353335

URL: http://dx.doi.org/10.1080/01442358209353335

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International Reviews in Physical Chemistry (1982), *2* (197–235)

RECENT APPLICATIONS OF HEAT CAPACITY MEASUREMENT IN PHYSICOCHEMICAL INVESTIGATIONS

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ABSTRACT

This review discusses the recent experimental heat capacity measurements which have been very useful in physicochemical investigations. Areas reviewed include critical point phenomena in systems such as fluids, magnetic systems, liquid crystals, co-operative Jahn-Teller transitions, etc. The uses of C_p measurements in the study of discrete energy levels in solids, in glasses at very low temperatures, in thin films and at high pressures are discussed. Calorimetric investigations in A-15 and other superconducting materials and applications of C_p measurements for evaluation of thermodynamic parameters in several new classes of materials are then briefly described. Finally, examples of applications of calorimetry in areas of biophysics, biological sciences and clinical medicine are cited. Two hundred and seventy references are cited and 25 figures are used for illustration.

INTRODUCTION

The measurement of heat capacity has been a useful technique of physicochemical investigation. The classical Dulong and Petit's law was instrumental in the estimation of atomic weights more than 150 years ago. The work of Einstein, Debye and Born, in the early part of this century, had shown the general relationships between the low temperature specific heat and the quantum theory of atomic and molecular motion. These early developments of the subject and the classical methods, such as adiabatic calorimetry, of measurement of specific heats have been comprehensively discussed by Gopal (1966) and by McCullough and Scott (1968). In addition, reviews by Kingery (1959), Keesom and Pearlman (1959), Marcus and Friedberg (1959), Kybett *et al.* (1968), Sturtevant (1970), Shelton (1975), McNaughton and Mortimer (1975) and Gonzalez (1980) are available for detailed discussion of specific areas of experimental calorimetry.

Though an established field, there has been a large amount of work in the past 10 to 15 years. During this time, large scale improvements were reported in the techniques of measurement. The recent methods such as a.c., pulse, relaxation and differential scanning calorimetry (DSC) have become very useful for measurements on newer classes of materials and under extreme conditions of pressure, temperature and sample geometry. Simultaneously, there has been widespread application of C_p measurements to understand physicochemical phenomena near second order phase transitions, at very low temperatures and in the fields of biology and medicine.

The present review is concerned mainly with the examples of important physicochemical phenomena and even biological phenomena wherein heat capacity measurements have played an interesting role—this covers a wide range of materials and experimental conditions. The level of presentation is such that a general acquaintance with the principles of thermodynamics and statistical mechanics, as applied to heat capacity studies is adequate. These principles and the simple models of molecular and lattice energy states are well known and the models allow a calculation of the heat capacities in simple cases. There are also semi-empirical calculations. The works of Partington (1949), Lee and Bigeleisen (1980), Takuechi (1980) are a few examples.

It is also known that heat capacity is a bulk measurement and from such a measurement it is often difficult to unambiguously elucidate microscopic details. A common example is the difficulty of separating the measured heat capacity into phonon, electron, magnon and other contributions (Gopal, 1966; Cracknell and Tooke, 1979). In this context one must mention the problems in the measurement itself which often has to be a painstaking task. During the past 10 years or so, considerable progress in the established conventional methods has taken place. Also newer methods like the a.c. method and the relaxation technique have been developed. These have been particularly useful in studies of newer materials available in small quantities or as thin films or foils and in measurements under high pressure, etc. Progress in the experimental methods up to the end of 1981 has been discussed in detail elsewhere (Lakshmikumar and Gopal, 1982).

SECOND ORDER PHASE TRANSITIONS

One of the striking applications of heat capacity measurements in recent times has been the study of second order phase transitions. The mean field theory of second order transitions was developed by Landau and others to give a unified picture of these transitions. However it was very easily noticed that many physical systems did not exhibit the mean field picture. For example, while the mean field theory expects the specific heat to be finite and discontinuous across the critical temperature T_c, early experiments on fluids and magnets showed that the specific heat was varying as

$$C_p = A\left|\frac{T-T_c}{T_c}\right|^{-0.1} + B\cdots$$

showing an infinity at T_c. The singularity is characterized by the exponent α in the specific heat measurements where

$$C_p = A\left|\frac{T-T_c}{T_c}\right|^{-\alpha} + B\cdots$$

Starting with the early 1960s, newer models for the phase transitions have been developed. The developments in theory due to Widom, Kadanoff and Wilson indicate the importance of fluctuations with the correlation length going to infinity as T_c is approached. These ideas form the basis for the Renormalization Group Theory of phase transitions (Kadanoff *et al.*, 1967; Fisher, 1974; Ma, 1976; Patashinskii and Pokrovskii, 1979; Fisher, 1979; etc). In this theory, every physical system has two important parameters.

1. The spatial dimensionality d of the system.
2. The symmetry of the order parameter n.

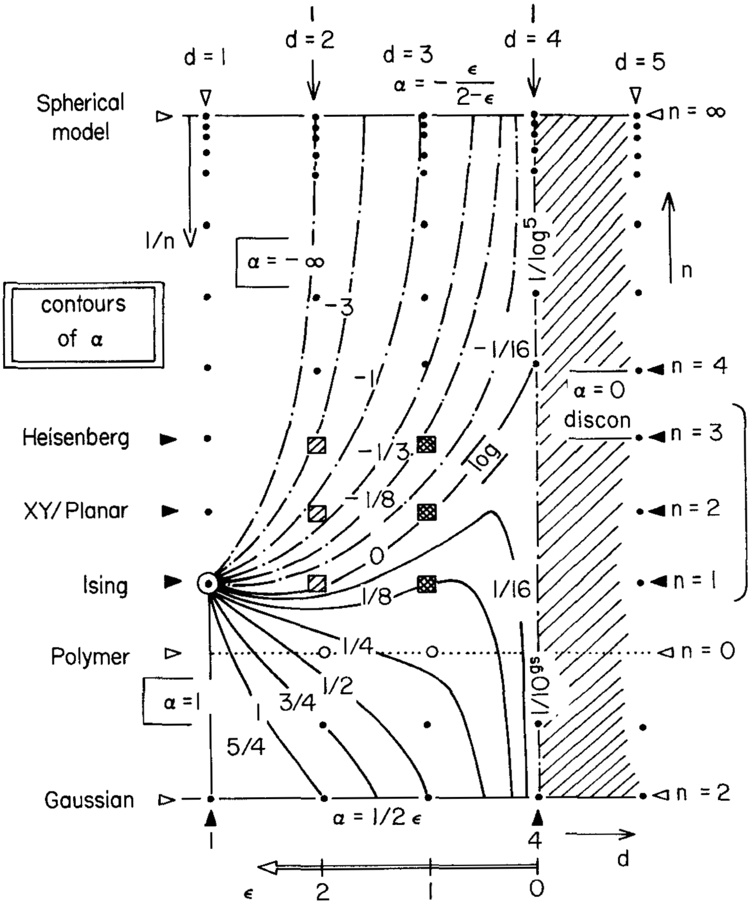

FIG. 1. Variation of the critical exponent, α, in the n, d plane (Fisher, 1974).

Systems with the same values of d and n are said to belong to the same universality class and the critical exponents are the same.

The most important exponents are: β the exponent for the order parameters; α the exponent for the energy (specific heat); and γ the exponent for the response function. The variation of α as given by these theories in the n, d plane is shown in *Figure 1*. The lines are for constant α values. In these calculations one starts with $d=4$ and results for other dimensions are obtained by perturbation calculations with the dimensionality being considered as $(4-\varepsilon)$ with ε being allowed to change continuously. It should be noted that the theory shows the mean field results for $d \geqslant 4$. These theories can be extended to more complex critical systems involving multicriticality. These aspects are discussed by Fisher (1979). The theory essentially gives a result that if

$$C_v = A^+|T-T_c|^{-\alpha} + \cdots \text{ for } T > T_c$$
$$= A^-|T_c-T|^{-\alpha'} + \cdots \text{ for } T < T_c$$

then $\alpha = \alpha'$ and

$$A^+/A^- = 2^\alpha \frac{n}{4}\Bigg[1+(4-d)+(4-d)^2 \left\{\frac{3n^4+74n^3+708n^2+224n+6400}{2(n+8)^4} + \frac{4-n}{2(n+8)}\zeta(2) - \frac{3(5n+22)}{(n+8)^2}\zeta(3) + \frac{9(4-n)}{4(n+8)^3}\zeta(-2.349)\right\}\cdots\Bigg]$$

Thus the amplitudes of the anomalies above and below T_c bear a universal ratio. The values are 1.324, 0.88 and 0.48 for $d=3$, $n=3, 2, 1$ respectively ($\alpha = -0.10$, -0.02 and $+0.08$ for $d=3$, $n=1, 2, 3$) (Gopal, 1981).

We note that here the C_p contributions from other sources, such as electrons, phonons, etc have to be subtracted to analyse the critical behaviour. As already mentioned, this is difficult and can be a source of error. The measurement of specific heats at phase transitions has been reviewed by Kerimov (1974), Westrum (1974), and Gronvold (1976). In the analysis of experimental results, particularly in solids, the influence of the impurities, strains and temperature gradients is quite drastic. An extremely interesting analysis of the effect of temperature gradients is by Ishibashi and Takagi (1975). The main results are shown in *Figure 2*. The figure shows the effect of a temperature gradient defined by a parameter s on a system which otherwise would have shown a singular C_p. Not only are the C_p data rounded off, but spurious side peaks also appear (*Figure 2*). Another example is the work on chromium near the Neel point by Williams, Street and Gopal (1979). The results shown in *Figure 3* show the large rounding off of the C_p peak due to strains introduced in the sample. The sample with maximum strain does not even show a small cusp.

The renormalization group theory is also used in a large number of other systems including polymers (e.g. Duplantier, 1980). The theory has been extended to establish phase boundaries for the first order transitions (Gartenhaus, 1981). Another interesting

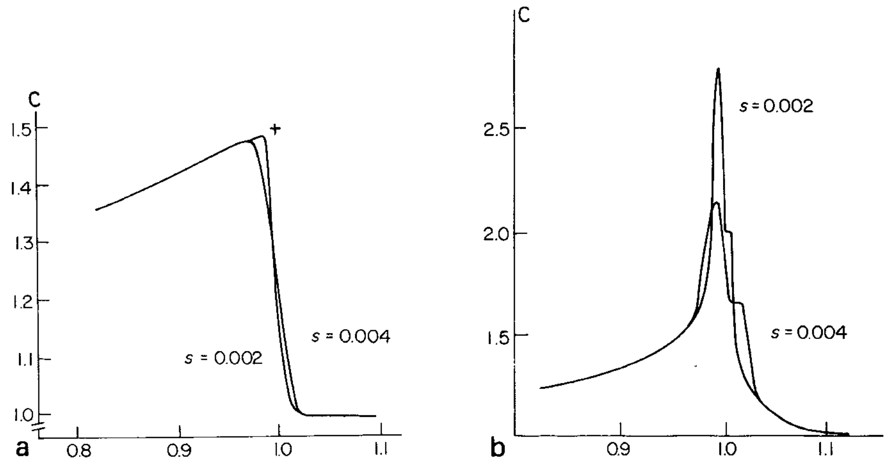

FIG. 2. Effect of temperature gradients on the C_p measurements near (a) an order-disorder transition and (b) for a λ-type transition for which side peaks appear. (s is a parameter characterizing the energy supply (Ishibashi and Takagi, 1975.)

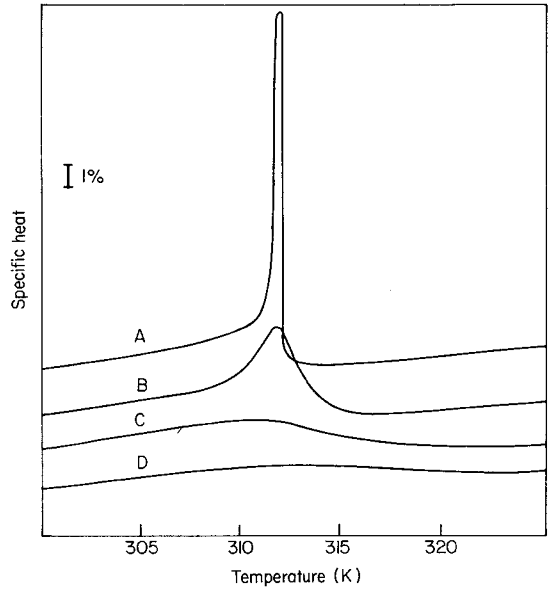

FIG. 3. The temperature variation of the specific heat of chromium in the vicinity of the Neel transition: A, annealed at 900 °C; B, rolled; C, annealed at 600 °C and D, swaged. (For clarity, curves have been displaced vertically and experimental points are not shown here.) (Williams, Street and Gopal, 1979.)

example is the study of critical slowing down of chemical reactions, where the reaction rate is seen to have γ as the critical exponent (Procassia and Gilterman, 1981).

Critical specific heats in fluids

Critical phenomena in fluids are characterized by $d=3$, $n=1$ and the theoretical ideal value of α is 0.11. When the sample temperature is close to T_c, as with the specific heat C_p, the compressibility K_T also shows a divergence. As a result, the small pressure head, $\Delta p = \rho g \Delta h$, across the sample of height Δh, which is normally negligible, is enough to cause a significant difference in density between the top and bottom layers of the sample. A detailed analysis of this is made by Moldover *et al.* (1979). Specific heat measurements have reached a stage of refinement to show these finer details also. A beautiful illustration of this is the work of Lipa, Edwards and Buckingham (1970, 1977) on CO_2. The effect of gravity is to round off the C_p peak as shown in *Figure 4*. The values of the exponents were evaluated for a sample of 1 mm height to reduce gravity effects. Initially, a value of $\alpha = \alpha' = \frac{1}{8}$ was reported. However, the more recent work with $t \sim 10^{-5}$ to 10^{-2} $[t=(T-T_c)/T_c]$ shows that $\alpha = \alpha' = 0.124 \pm 0.005$ and $A^+/A^- = 0.54$. These confirm the RNG calculations for the Ising model.

Perhaps, the most accurate C_p data in fluids are reported at the λ point of liquid He^4. The original data of Buckingham and Fairbank (1961) were extended and improved by Ahlers, from $t=10^{-5}$ *to* $t=10^{-7}$. He reports, $\alpha = -0.05$. The measurements of C_v and dC_v/dT show that A^+/A^- is a constant independent of pressure (Okagi and Watanabe, 1978). The results of the measurements on He^4 are reviewed by Ahlers (1980). The main results are shown in *Figure 5*. The recent RNG calculations of Chang and Houghton (1980) regarding the amplitude ratio A^+/A^- are in excellent agreement

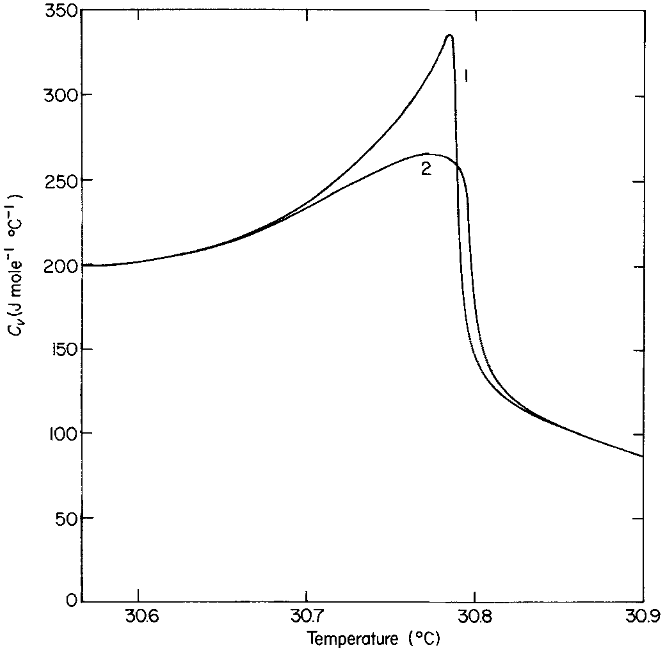

FIG. 4. Influence of gravity on C_v of CO_2 in the critical region: 1, sample height = 1 mm; 2, sample height = 14 mm (Lipa, Edwards and Buckingham, 1977).

with Ahler's data. Another interesting experiment on He^4 adsorbed on Vycor glass shows that the superfluid density of the adsorbed gas $\rho_s \sim (1.955 - T)^{0.65}$ as in bulk He^4 (1.955 K is the T_λ of He^4 adsorbed on Vycor glass). However, the C_p measurements do not show any anomaly (Joseph and Gasparini, 1978). Bloemen, Thoen and Van Dael (1980, 1981) have reported some new interesting results on liquid mixtures. They studied the trimethylamine–water system with $t \sim 10^{-5}$ and find $\alpha = \alpha' = 0.110 \pm 0.004$ and $A^-/A^+ = 1.79$. They also find that addition of 0.07% ethanol shows renormalization effects and the value of α shifts as theoretically expected. Experiments were also done with D_2O and the results are generally in good agreement with the theory.

Order–disorder and magnetic phase transitions

The study of the critical specific heats at the order–disorder transitions has been pursued for many years. Early measurements were reported by Sykes and Wilkinson (1937) and Moser (1937) for the CuZn system. These data based on the adiabatic calorimetry were later improved by Ashman and Handler (1969). They used the a.c. method and reached $t \sim 10^{-6}$. For $T > T_c$, $\alpha = 0.13 \pm 0.01$ and $A^+ = (1.09 \pm 0.06)\,R$ were reported. For $T < T_c$ they observed a logarithmic singularity, $\alpha' = 0.01 \pm 0.01$, $A^- = (0.53 \pm 0.04)$ R. Thus the system shows Ising behaviour only for $T > T_c$.

Measurements on EuTe, T_N (Neel temperature) = 9.81 K and EuSe, $T_N = 4.60$ K were also reported (Johanson and McCollum, 1980). Only data for EuTe were analysed as the rounding off errors were much larger for EuSe. They report, $\alpha = \alpha' = 0.08 \pm 0.006$ and $A^+/A^- = 0.75 \pm 0.14$ for t in the range 0.005–0.06. Lederman, Salamon and

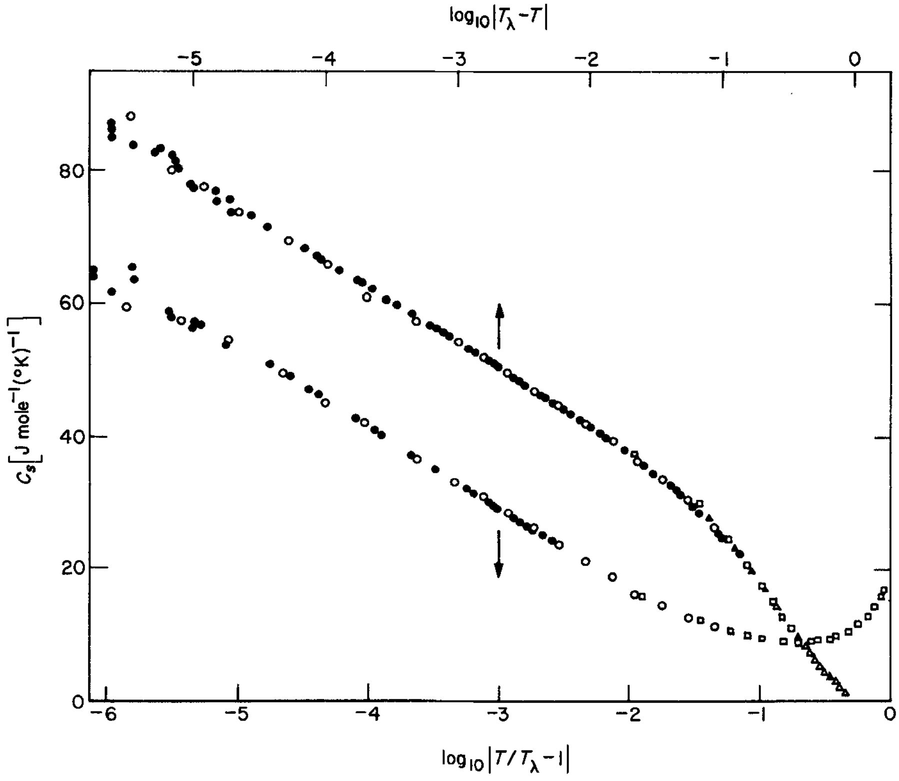

FIG. 5. Heat capacity at saturated vapour pressure of liquid ^{4}He near T_λ as a function of $\log_{10}|T/T_\lambda - 1|$. The upper set of data is for $T < T_\lambda$ and the lower set is for $T > T_\lambda$ (open circles, Buckingham and Fairbank, 1961; solid circles, Ahlers, 1980).

Shacklette (1974) have reported the measurements on $RbMnF_3$, Fe, Ni and CuO. They generally find $\alpha = \alpha' = 0.110$ as expected. The garnet DAG was investigated by Wolfe and co-workers (Keen, Landau and Wolfe, 1967). When measurements with 50 μK temperature resolution were made, the maximum in C_p is found to have been rounded off by 2–3 mK, causing severe problems. To analyse the data different values of T_N, had to be used above and below the critical point. For $T < T_N$ a logarithmic singularity is noted. Some of the deviations from the expected Ising behaviour were also explained by Wolfe *et al.* (1972).

Another system where rounding off errors were severe was Gd. Values of $\alpha = 0.09 \pm 0.05$ and $\alpha' = 0.35 \pm 0.05$ were reported (Lewis, 1970). However, rounding off could have been a cause for $\alpha \neq \alpha'$ as $\alpha = \alpha'$ is also a possible fit. This experiment clearly shows the complexity involved in the analysis. To study Gd in a better way, Simons and Salamon (1974) tested the proportionality ΔC_p vs Δ $(d\rho/dT)$ in magnetic fields. The existence of this proportionality was seen to be a proof of the Fisher Langer model. Recently thermal expansivity measurements on single crystal Gd have led to the speculation that Gd does not behave as a Heisenberg ferromagnet and that the singularity in expansivity seems to be a discontinuous transition (Robinson and Lanchester, 1978). Specific heat measurements of Lanchester *et al.* (1980) on single crystal Gd seem also to agree with the model of a discontinuous transition but the problem is still open.

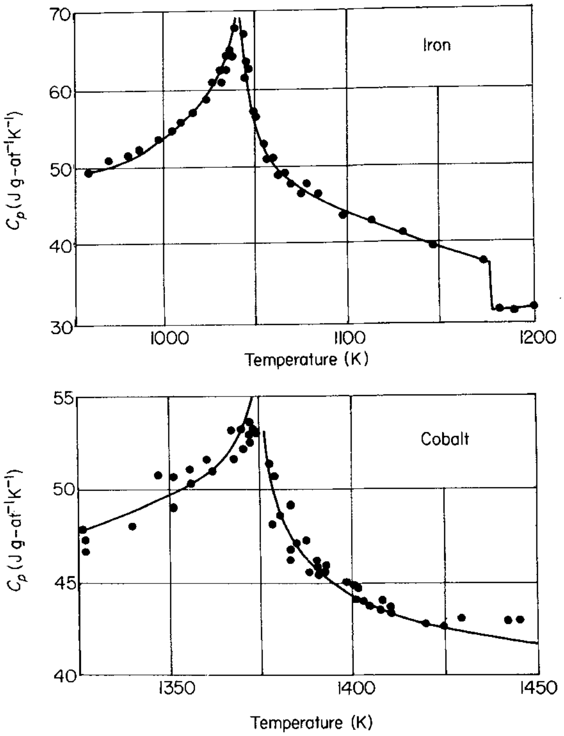

FIG. 6. Specific heats of iron and cobalt near the Curie point (Kraftmakher, 1973).

Measurements on Fe by Kraftmakher and Romashina (1966) indicate $\alpha = \alpha' = 0$ and $A^+/A^- \neq 1$. The results on Fe and Co using a.c. calorimetry are shown in *Figure 6* (Kraftmakher, 1973). Experiments on MnF_2 are very interesting. Values of $\alpha = \alpha' = 0.12$ and $A^+/A^- = 0.5$ are reported (Nordblad *et al.*, 1981) for t in the range 10^{-5}–10^{-3} confirming the Ising model. The interesting feature is that away from T_N, there is speculation of a change in spin dimensionality from $n = 1$ *to* $n = 3$. Also when doped with Fe, the essential shape of the C_p curve does not change. Measurements on a number of magnetic systems at low temperatures using high resolution isothermal shield calorimetry (*see* Lakshmikumar and Gopal, 1982 for details of the method) were reported by Rives (1972).

Recently ferromagnetic metallic glasses have been studied. Schowalter *et al.* (1977) have reported $\alpha = \alpha' = 0.18 \pm 0.04$ and $A^+/A^- = 1.2 \pm 0.3$ for the metallic glass $Fe_{75}P_{15}C_{10}$. The results are seen in *Figure 7*. However, for the metallic glass $Fe_{34}Ni_{46}P_{20}$, no anomaly in C_p was noted where dR/dT data show $\alpha = \alpha' = 0.065 \pm 0.05$ (Craven, Tsuei and Stephans, 1978). Ikeda and Ishikawa (1980) have analysed the position and shown that the sharp peak in C_p is exhibited only at some compositions. They suggest that there are local variations of T_c responsible for the observed behaviour.

Ferroelectrics

Phase transitions in ferroelectrics are more complex than in other systems. In many ferroelectrics, finite values of ΔH and ΔS are observed at the transition to the

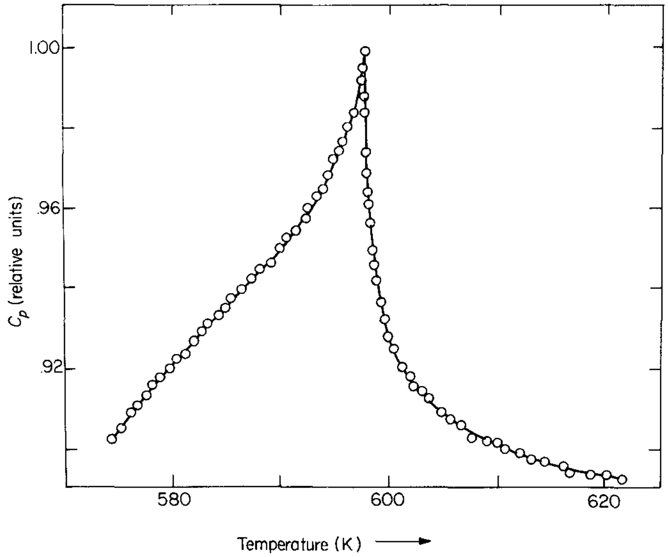

FIG. 7. Specific heat of amorphous $Fe_{75}P_{15}C_{10}$ relative to the maximum at T_C plotted as a function of temperature (Schowalter *et al.*, 1977).

paraelectric phase. Also many systems, exhibit only the mean field behaviour. Improper ferroelectrics and incommensurate phase transitions have added to the complexity of the subject. In many cases C_p data at these transitions, are not accurate enough to analyse the critical behaviour (Gronvold, 1976). This is true of even recent work (e.g. Ajgoankar and Deshpande, 1981; Deutsch and Litov, 1974). A few interesting examples are discussed here. $PbHPO_4$ was studied by Lopez, Tello and Jubindo (1981), here $\Delta H = 63.2 \pm 0.3$ cal/mol and $\Delta S = 0.22 \pm 0.007$ cal/mol K at $T_c = 307.75 \pm 0.03$ K. However, for $0.1 < T_c - T < 0.3$ K and $0.2 < T - T_c < 5$ K values of $\alpha = \alpha' = 0.08 \pm 0.022$ are noted. This is an example of the co-existence of a ΔH and an exponent. Several materials, the classic example being TGS, show Landau behaviour (e.g., $AgNa(NO_2)_2$, $KFe(MoO_4)_2$, $NH_3(CH_2)_n$-NH_3CdCl_4 ($n = 3, 5$), etc) (Helwig, Petterson and Schneider, 1978; Smolensky *et al.*, 1980; Fouskova, 1980). Generally uniaxial ferroelectrics alone are expected to show mean field behaviour. An attempt to dope TGS with D_2 and observe the change from uniaxial behaviour was not successful. With 47% D_2, the classical behaviour was still noted (Muser, Helwig and Barth, 1980).

The complete nature of the incommensurate-proper phase transition is not understood (Fisher, 1979). Rb_2ZnCl_4 shows an incommensurate-normal phase transition at 303 K which is reflected as a second order phase transition in C_p (Choudhari *et al.*, 1980), and in expansivity (Krishnapur, Lele and Subramanyam, 1980). Lopez *et al.* (1980) in a more detailed analysis showed that the transition at 303.56 K is of the Ising XY type with $\alpha = \alpha' = 0.02 \pm 0.02$ for C_p and that $\beta = 0.37 \pm 0.003$. The range of the critical behaviour is large, of the order of 30 K. More precise experiments on the phase transitions in ferroelectrics are obviously necessary for a more detailed understanding of the area.

Phase transitions in liquid crystals

It is well known that liquid crystals exhibit a large number of ordered phases where the nature of ordering is quite complex. The transitions between the nematic, smectic A and smectic A, smectic C phases have attracted considerable attention following the prediction of de Gennes (1972) that these are continuous with the $d=3$, $n=2$ Ising XY model being applicable. The common features between He^4 and liquid crystal transitions are of interest. As in the case of ferroelectrics, in some experiments, ΔS and ΔH are observed, for example in liquid crystal DMC (Andrews and Bacon, 1974). However, in 8S5, ΔS is as low as 0.002 R (Shantz and Johnson, 1978). For 8OCB, values of $\alpha=\alpha'=0.24\pm0.03$ and $A^+/A^-=1.01$ were reported for t in the range 3×10^{-5}–4×10^{-3} (Viner and Huang, 1981). However, Shantz and Johnson (1978) show that the liquid crystal 8S5 has $\alpha=\alpha'=-0.54\pm0.07$ which is not the expected XY model value. Measurements of Ostrovskii *et al.* (1978) were not conclusive and α is estimated as 0.2–0.3. Le Grange and Mochel (1980) have attempted to clarify the problem and found that in 8OCB, two different samples gave $\alpha=\alpha'=0$ and $\alpha=\alpha'=0.25$ (*see Figure 8*). They suggest that there is possibly a multicritical point or that there is 'cross over'. They show that small chemical and compositional differences can affect the data. For the system 8CB, α is found to be 0.30 ± 0.05. At high pressures, the peak was smaller but the general shape is the same (Kasting, Garland and Lushington, 1980). They point out that if there is a cross over from tricritical to XY behaviour, the insensitivity of α to t and to pressure is not explained. As at present, de Gennes' conjecture seems probable but no final experimental proof is available.

Cooperative Jahn-Teller transitions

The Jahn-Teller theorem is concerned with the interaction of the energy states of the rare earth ion and crystal fields. The cooperative transitions involve a change of crystal symmetry taking place at low temperatures to reduce the energy of the ion. These effects are reviewed by Gehring and Gehring (1975) and the changes in elastic constants due to the transitions by Melchev (1976). Examples of these systems are rare earth zircons such as $DyVO_4$, spinels such as $CuFe_2O_4$ and rare earth pinictides such as DySb. These transitions can generally be explained by mean field theories. Specific heat measurements exist for $TmVO_4$, $TmAsO_4$, $TbAsO_4$, $DyVO_4$, $Tm_{1-x}Lu_xVO_4$, etc. (Cooke, Swithenby and Wells, 1972; Wells and Worswick, 1972; Ivanov *et al.*, 1979). Generally a mean field type discontinuous change is observed. However, in $TmVO_4$, there is no tail at high temperatures above the transition in contrast to $DyVO_4$ (*see Figure 9*). It is seen that the forces are very much short range in $TmVO_4$ and the electrons are strongly coupled to the strain modes. In $DyVO_4$, there is long range interaction, and coupling to other modes is also important (Gehring and Gehring, 1975). A new interesting example of *J*–T transitions is due to Salamon (1979a). The phase transitions in superionic conductors $RbAg_4I_5$ at 209 K, KAg_4I_5 at 194 K and $NH_4Ag_4I_5$ at 199 K with $\alpha=\alpha'=0.15\pm0.01$ and $A^+/A^-=0.69\pm0.01$ show the 3*d* Ising model behaviour and the cause of the transitions is suggested to be *JT* interactions of the lattice and Ag^+ ion.

Super ionic conductors

The super ionic to normal ionic phase is a transition of the first order in several systems. In some cases however, a mean field type second order transition is noted. The basic properties of super ionic conductors are reviewed in the monograph edited by Salamon (1979). In super ionic conductors (SIC) of the Rb, K, $NH_4Ag_4I_5$ family, second order transitions are noted. In all systems, $\alpha=\alpha'=0.15$ and $d\sigma/dT$ is found to be proportional to the specific heat, as expected from the theory (Vargas, Salamon and Flynn, 1978) of

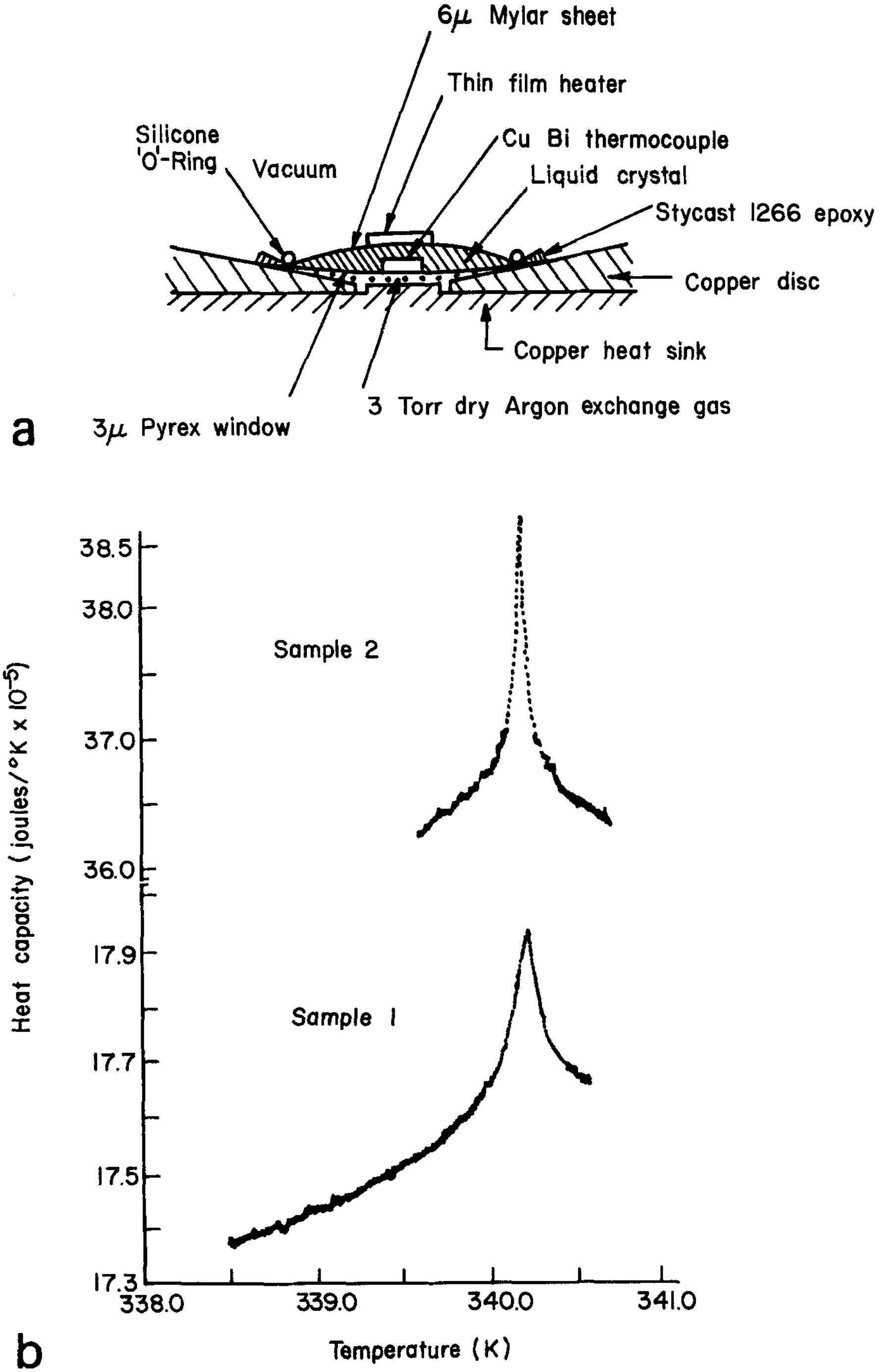

FIG. 8. Specific heat measurements on liquid crystals, (a) sample geometry for a.c. calorimetry and (b) variation of C_p for two samples which show exponent values $\alpha=0$ and $\alpha=0.25$ (LeGrange and Mochel, 1980).

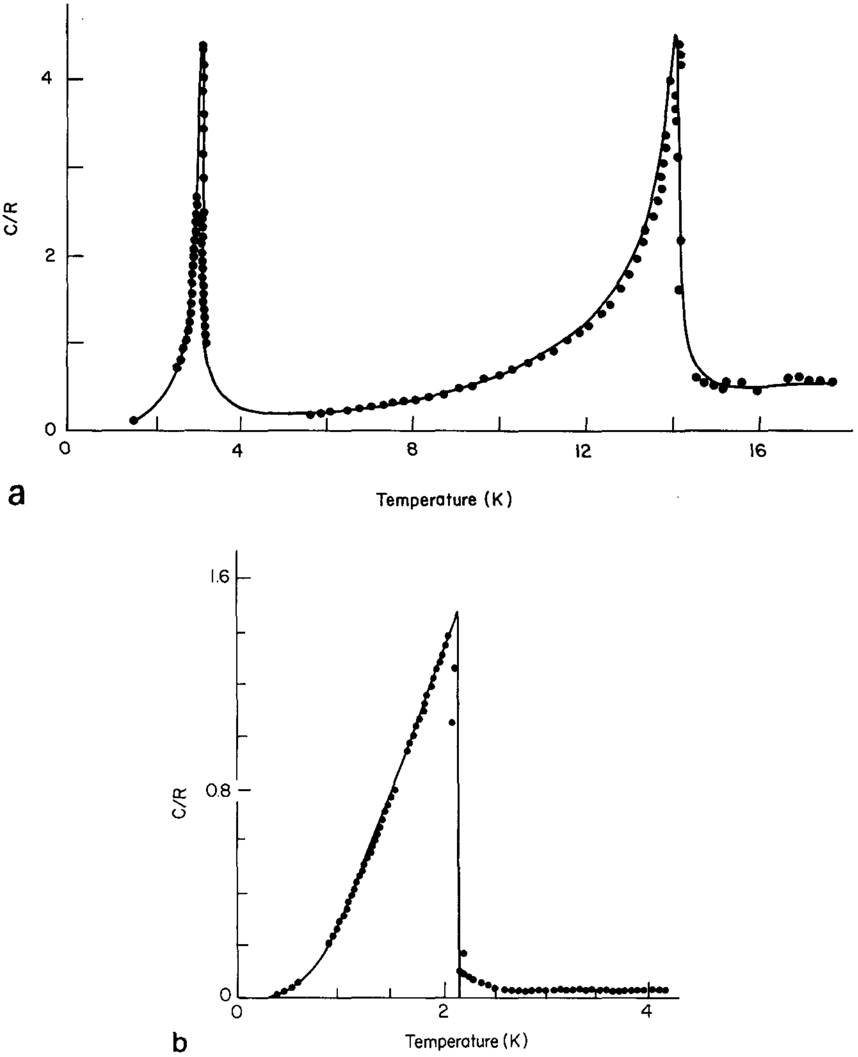

FIG. 9. Variation of C_p near the Jahn-Teller phase transition for $DyVO_4$ and $TmVO_4$. The high temperature tail in $DyVO_4$ indicates the existence of long range interactions (Gehring and Gehring, 1975).

the Ising model. In $(C_5H_5NH)Ag_5I_6$, there is a slow onset of disorder in Ag^+ ions from -30 °C to $+50$ °C. There is a possible second order transition at 220 K (Himba, 1977). A λ-type transition in $RbAg_4I_5$ is found by Johnston, Weidersich and Lindberg (1969). They find a classical behaviour with a small tail at higher temperatures and a first order transition at 121.8 K. Pardee and Mahan (1974) find that $RbAg_4I_5$ shows a logarithmic singularity for $T < T_c$ and that there is no anomaly for $T > T_c$. The $\alpha \neq \alpha'$ result is not explainable. The C_p measurements on CaF_2 structure super ionic conductors show a transition at high temperatures. A recent analysis has shown that this is not a first order transition (Derrington, Navrotsky and O'Kaffee, 1976). $H°$ is determined over a wide temperature range and is seen to be a sigmoidal curve with maximum slope at 705 K. σ shows a small change at 705 K. The authors conjecture a possible slow onset of disorder of the ions. For solids of the CaF_2 structure, high temperature excess C_p in CaF_2, PbF_2, $SrCl_2$, etc is also explained as a contribution from Frenkel-type defects (Oberschmidt, 1981). The general features of phase transitions in the super ionic conductors can be explained by models based on the Landau theory (Salamon, 1979).

STUDY OF DISCRETE ENERGY LEVELS IN SOLIDS

It can be easily seen that the introduction of a set of discrete energy levels into a system would cause a peak or broad maximum in C_p at $kT \approx \Delta E$ where ΔE is the separation of the levels. The famous example of this is the Schottky anomaly (Gopal, 1966) and a few recent interesting examples are discussed here. Measurement of C_p of NaF has shown that there is an anomalous peak in C_p at $T < 0.6$ K (Harrison, Lombardo and Peressini, 1968). This peak for two samples is analysed and shown to be due to 0.1 and 0.3 ppm of OH^- impurity (*see Figure 10*). This is an example where a specific heat measurement, in spite of being an average over all the energy states of the system, identifies a very low concentration of impurity, which is not easily detected by other methods. In NaF the $\theta_D(C_p)$ is 466 K while θ_D (elastic) is 491 K. The discrepancy is not understood since, for most alkali halides, the agreement between the two θ_D values is good.

Other examples of low temperature Schottky anomalies are CH_2D_2 and CD_4. In CH_2D_2 the anomaly is consistent with the energy level calculations (Lushington and Morrison, 1978). In CD_4, the anomaly corresponds to a splitting of 0.042 ± 0.01 K and is shown to be not due to impurities (White and Morrison, 1980). The anomaly is due to tunnelling states arising out of nuclear spin and symmetry. Some evidence for these states is obtained from neutron scattering. On the other hand in Gd_2O_3 an anomaly is

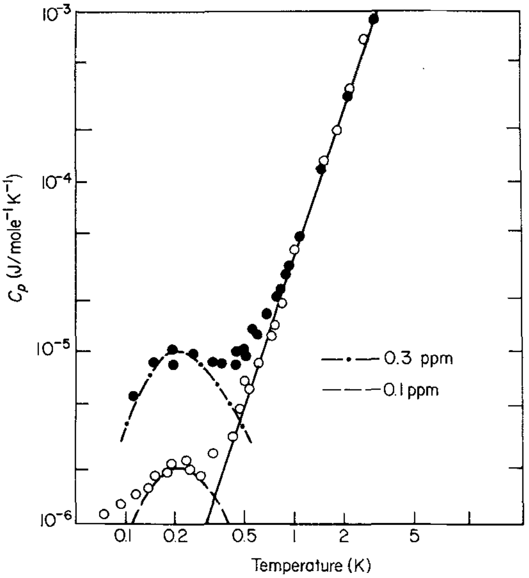

FIG. 10. Specific heat of NaF as a function of temperature. Theoretical Schottky anomaly contributions for 0.1 ppm and 0.3 ppm concentrations of the impurities are also shown (Harrison, Lombardo and Peressini, 1968).

seen at 2 K. This is probably not due to the splitting of Gd ion states since this is not corroborated by ESR. There are two possible states for Gd, one set of which is coupled by anti-ferromagnetic ordering, causing the anomaly (Stewart, Barclay and Steyert, 1979). Cubic Gd_2O_3 is an interesting case as it has possible applications for magnetic cooling. Low temperature Schottky anomalies are also found in rare earth sulphides $RS_{1.5}$ (R = La, Ce, Pr, Nd, Gd, Th, Dy, Ho, Er, Tm or Lu) (Ho *et al.*, 1978). In the case of $NdS_{1.5}$ and DyS the data corroborate optical experiments. Similarly in the mixed valence systems, SmS and SmSe, an anomaly caused by the splitting of Sm^{3+} states at ~2.4 K is noticed (Coey *et al.*, 1979).

Lyon and Westrum (1974, 1974a) have measured C_p of $ZnWO_4$ and $FeWO_4$. They determined the thermodynamic parameters, C_p, S^0, H^0 and $(G^0(T)-H_0^0)$. On subtracting magnetic and other contributions, an excess C_p is noted. This is attributed to a Schottky anomaly with a separation of the two levels by 1510–2700 K, which is very large. $Fe(NiMn)_{0.5}$ alloys also show Schottky anomalies at 400 K. The ferromagnetic $Fe_{1-x}Ni_x$ alloys show Schottky peaks at 1.5–3 K (Bendick, Ettwig and Popperhoff, 1978).

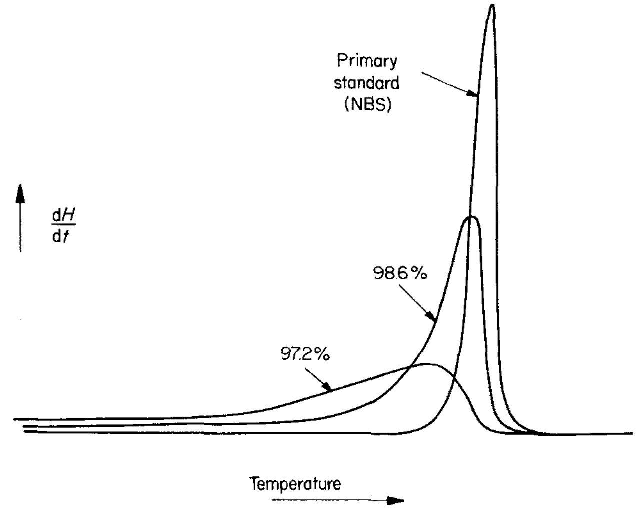

FIG. 11. Effect of purity on melting endotherm of benzoic acid (McNaughton and Mortimer, 1975).

In a recent experiment, Cotts and Anderson (1981) show that pure copper shows an anomalous low temperature C_p. However, the concentration of impurities required to show an anomaly of the observed magnitude is much larger than the known levels of magnetic and other impurities present. Here is another example of C_p data being sensitive to small concentrations of impurities. At this point one can mention that the use of calorimetry for purity evaluation is not new (Smit, 1957; Kybett *et al.*, 1968). The development of the DSC has added a new calorimetric tool for this purpose. A way of routine purity evaluation is discussed by McNaughton and Mortimer (1975). The main idea is shown in *Figure 11.*

SPECIFIC HEATS OF GLASSES AT LOW TEMPERATURES

This is a new example, where C_p measurements on fused quartz have opened a new area of work. It was noted by Zeller and Pohl (1971) that fused quartz, a good insulator, shows an anomalous linear contribution to C_p (like the electronic contribution). The origin of this excess term was not clear for some time. It was then shown by Anderson, Halperin and Varma (1972) and Phillips (1972) that if one postulated the existence of tunnelling states with an asymmetric potential well, with two minima and assumed the energy barrier to be random, the linear term can be explained. Zackle (1972) showed that corresponding to this, anomalous behaviours in ultrasonic velocity and attenuation are expected. Also the model predicts a T^2 term in the thermal conductivity.

The experiments among others by Stephans (1973) on C_p, Bellessa and Bethoux (1977) on ultrasonic velocity and Graebner *et al.* (1977) have confirmed the basic model. The linear excess C_p term is clearly shown in *Figure 12*. The general features of the model have been reviewed exhaustively (Hunklinger, 1978; Bhattacharya, 1981; Black, 1978; Lohneysen, 1981; Phillips, 1981). However, soon after the proposal of the model, it was realized that the density of the tunnelling states estimated from ultrasonic measurements and from specific heat measurements were very different. This meant that some of the tunnelling states should be contributing to C_p only. A mechanism of thus explaining the experiments was discussed by Heinrichs and Kumar (1976). However, the consistency is not completely resolved (Black, 1978). Loponen *et al.* (1980) tried to resolve this by making C_p measurements on very short time scales. They

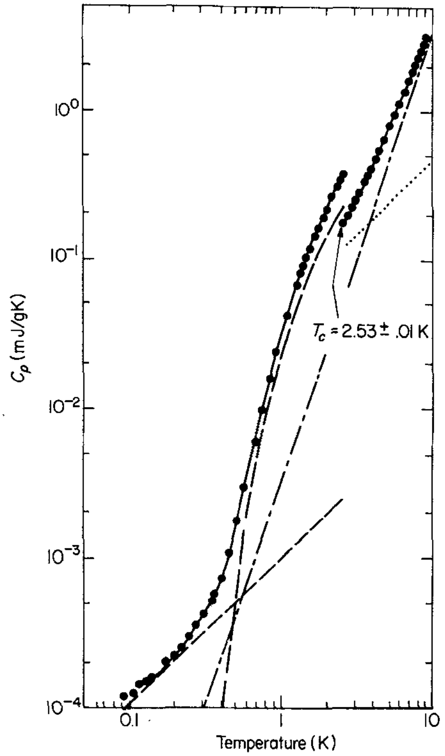

FIG. 12. Heat capacity of the superconducting disordered metal $Zr_{0.7}Pd_{0.3}$. The solid line is a fit to the data using standard theory. The individual components are indicated as follows: .... electrons above T_c; ---- electrons below T_c; —·—· phonons; and ——— extra contribution linear in T (Graebner *et al.*, 1973).

improved the earlier experiments where no departure from d.c. value was seen (Kummer, Dynes and Narayanamurti, 1978). The newer experiments made direct C_p measurements rather than diffusivity measurements. They show that the states contributing to the $C \sim T$ term decouple at 10 ms and 1 K. There is however an excess Debye term. The cause of this is not clear. These experiments are the first, where the decoupling of the tunnelling states is noticed. The decoupling is shown in *Figure 13*.

The origin of these states is not yet clear. Studies by Klein *et al.* (1978) and others show that there is a heuristic analogy to the strain interactions (Fisher and Klein, 1979). Smith (1979) has shown that these states are observed in computer models of network glasses. Measurements on polymers (Bhattacharya, Smith and Anderson, 1979), epoxy resin (Kelham and Rosenberg, 1981), glycerol (Calemczuk, Lagneir and Bonjour, 1979), etc have shown the existence of these states in different types of glasses making them universal to the glassy state. Recent measurements at very low temperatures on

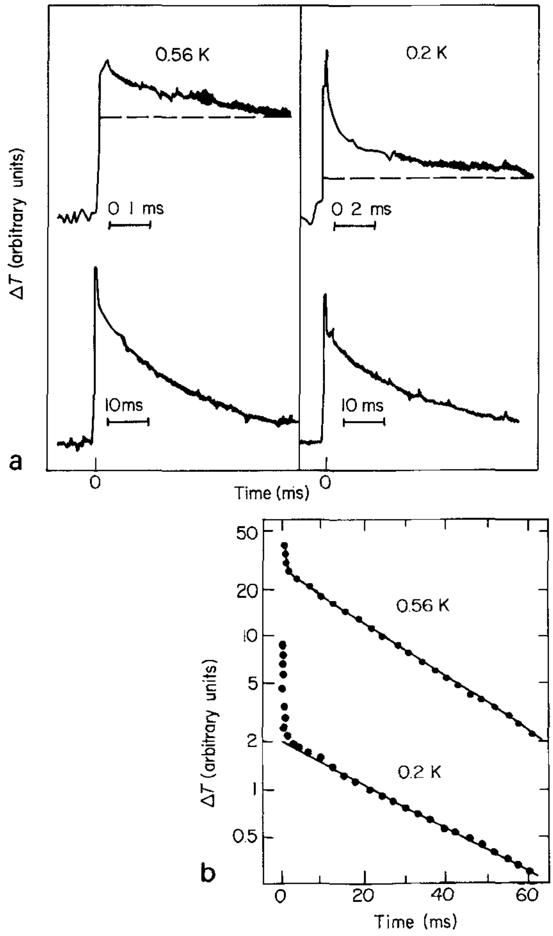

FIG. 13. Variation of the C_p value when experiments are performed in very short time scales. (a) At two temperatures, the effect of a short time heat pulse is different. (b) The variation of $\Delta T(t)$ is logarithmic at long t only showing change of C_p (Loponen *et al.*, 1980).

glassy Ge films have shown that the contribution is very much smaller (Lohneysen and Schink, 1982) but this is expected for these glasses with very open structures (Phillips, 1972).

Experiments on irradiated crystalline quartz have shown that defects in SiO_2 (basically trapping of a hole near an oxygen atom) interact with the strains and random electric fields and give rise to similar terms (Saint Paul, 1980; Gardner, 1981). Similar observations on the possibility of such behaviour in crystalline materials were earlier made by Phillips (1978). While these results seem to support the tunnelling model there are several other models in use as discussed very recently by Phillips (1981). Basically, this area is a beautiful example of the insight into physicochemical phenomena that is directly based on C_p measurements to a large degree.

A-15 MATERIALS—TRANSFORMATIONS AND STABILITY

A-15 materials with their high T_c values are extensively studied, the interest being sustained by possible applications (Muller, 1980). C_p measurements have been particularly useful in the analysis of transformations and stability of A-15 phases. The cubic to tetragonal martensitic transformation was first noticed in V_3Si where this transformation leads to small peaks in C_p data. *Figure 14* shows the typical results. The A-15 samples, Nb_3Sn, V_3Si, V_3Ga and Nb_3Al were studied by Viswanathan and co-workers. In all these systems, small peaks are noted in the C_p data (Viswanathan, 1974; Viswanathan and Johnston, 1973, 1976, 1976a; Viswanathan *et al.*, 1974). However, Abou-Ghantous *et al.* (1981) observed that V_3 Si shows the martensitic transformation only for some samples at 20 K, i.e. above $T_c = 17$ *K*. These authors suggest that there is no complete cubic-tetragonal phase transformation. There is only connectivity in tetragonal regions and the peaks in C_p data are due to a small spread in T_c values. This explains the higher $\Delta C_p/T_c$ value for non-transforming samples. The effect of plastic deformation on pure Nb was also studied through calorimetry (Zubeck *et al.*, 1979). The parameters of interest are $[\Delta C_p]_{T_c}$ and the Ginzburg Landau parameter K . $K = K_0 + 7.5 \times 10^{-3} \times \gamma^{1/2} \rho_\gamma$. At H = 0, the width of transformation in C_p increases with the deformation. Also K and ΔK increase with deformation. The total C_p of the mixed state is then analysable in terms of a spread in K.

Irradiation damage of A-15 phases has also been studied (Mueller *et al.*, 1976; Pande and Viswanathan, 1978). The latter have analysed the defects in A-15 materials caused by irradiation. They show that defects causing static displacement as well as anti-site defects co-exist in small (20–60 Å) domains. The long range order parameter S has smaller values in these domains but the A-15 structure is retained. The γ values and the phonon spectrum details of A-15 phases such as Nb_3(Ir–Pt–Au) and V_3(Ir–Pt–Au) (Junod, Bichsel and Muller, 1979), $Nb_{0.2}Zr_{0.8}$ (Gmelin and Guckelsberger, 1980), $Nb_3Al_{0.83}Ge_{0.21}$ (Stewart, Szklarz and Giorgi, 1978), etc, are also reported.

Stewart, Newkirk and Valencia (1980), in a recent experiment showed that Nb_3Nb is stabilized in the A-15 phase by 1% of Si or Ge. This A-15 stabilization was previously known only for W with 5% impurity. The T_c,$\gamma C_p/T_c$ and density of states values for various compositions of Ge (0.06–0.29%) and Si (0.39–0.54%) were determined. Pure Nb_3Si in A-15 phase is expected to have a T_c of 22–38 K. While the pure phase is not known, Stewart, Olinger and Newkirk (1981) have recently formed a compression formed Nb_3Si with about 70% A-15 phase with T_c of 18 K. The C_p data were determined and if the contribution to γ from the tetragonal Nb_3Si and bcc Nb are subtracted, one obtains a T_c of 20.5 K which is very encouraging.

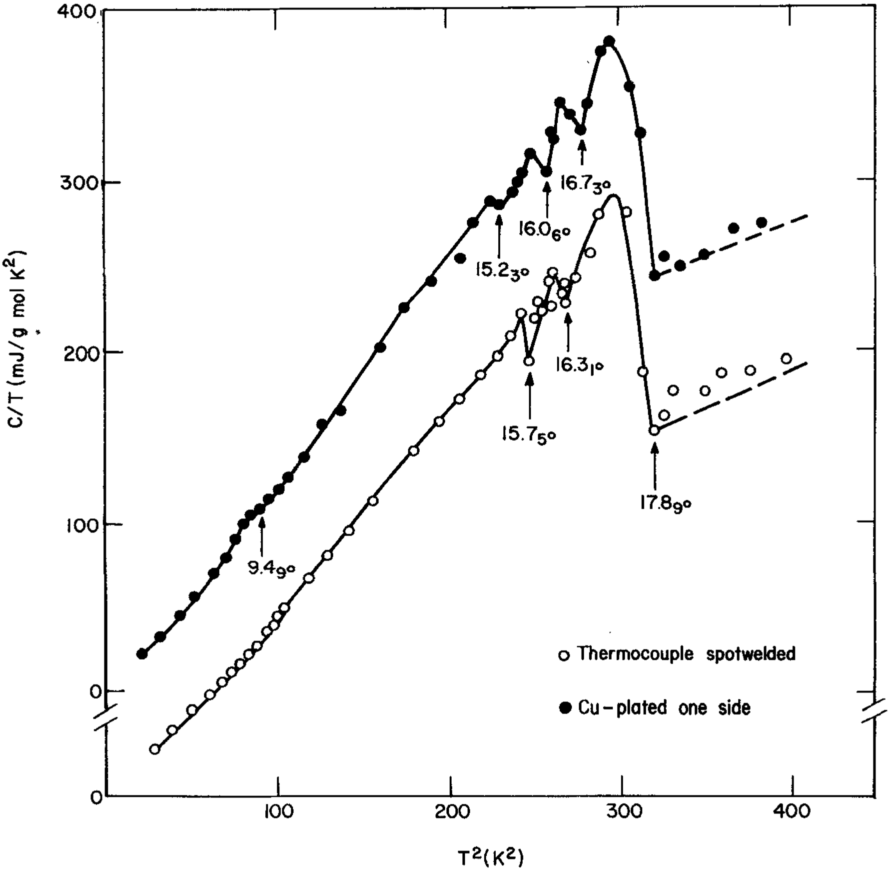

FIG. 14. Heat capacity data up to ~20 K for a vapour-grown polycrystal of Nb_3Sn of mass 30 mg. For a first measurement of this sample (○), the thermocouple temperature sensor was attached to the sample by spot welding. The second measurement (●) was carried out after an additional thin layer of copper was applied to one side of the sample (the data have been corrected for the contribution due to the copper layer). For clarity, the latter data set is displaced upward by 50 mJ/g mol K^2 (Viswanathan and Johnston, 1976).

CALORIMETRIC STUDIES OF SUPER CONDUCTORS

In addition to transformations in A-15 materials, calorimetry is used for other investigations on super conductors (Knapp, 1978). One of the important parameters is the strong coupling parameter, λ related to γ by

$$\gamma = \tfrac{2}{3}H^2K_B^2N(E_F)(1+\lambda) = \gamma_{bl} + \gamma_1$$

Since $\gamma_1 \rightarrow 0$ at high temperatures, we can determine λ through C_p measurements. Knapp (1978) reviews λ values of V, Nb, Ta, etc which are useful in a data analysis of A-15 materials. The θ_D values of A-15 materials also show softening at low temperatures. High T_c values are also reported for the C-15 materials (e.g. $V_2Hf_{1-x}Ta_x$).

These materials show large changes in C_p at the transformation (structural) at ~ 100 K (Halfstrom, Knapp and Aldred, 1978).

The molybdenum chalcogenides are another group of interesting super conductors. These materials show a large C_p at low temperature and no softening of θ_D. This indicates that the neutron diffraction picture of considering Mo_6S_8 units as quasi-rigid units, bound loosely to each other and to X atoms, is correct. Under this picture, the XMo_6S_8 can be considered as a molecular crystal (Bader *et al.*, 1976). The properties of these materials are reviewed by Alekseevski (1980) and Nalini and Amritkar (1980). Some of the high T_c super conducting examples are $PbMo_6S_8$ (15 K), $Cu_2Mo_6S_8$ (11.3 K), $Ga_4W_4PbMo_6S_8$ (14.9 K), etc. The variation of H_{C_2} for these is the same as A-15 materials

$$H_{C_2}=H_{C_2}(0)\times\left[1-\left(\frac{T}{T_c}\right)^{3/2}\right]$$

The $H_{C_2}(0)$ values are also very high for these materials (e.g. 580 KOe for $Ga_4W_4PbMo_6S_8$).

These materials show an Einstein mode contribution and

$$C_p=\gamma T+AC_E+BC(\theta_D)$$

If one determines

$$\gamma(H)=\frac{dH_{C_2}}{dT}\times\rho^{-1}\times 2.2\times 10^{-5}$$

one finds that $\gamma(H)<\gamma(C_p)$ for the materials showing θ_E contribution. For $NaMo_6S_8$, $CuMo_6S_8$, etc, no θ_E term is found, also $\gamma(C_p)\sim\gamma(H_{C_2})$. But the $H_{C_2}(0)$ value is low. These materials also show co-existence of the super conducting and magnetic ordering. $YbMo_6S_8$ for example shows a λ-type C_p maximum at $T_N<T_c$, where there is antiferromagnetic order. The $GaMo_6S_8$ shows a sharp peak in C_p at 45 K which is supposed to be a structural transition. There is also a magnetic transition at 20 K. C_p data on a series of La, Cu, Y, Sc compounds show that only YMo_6S_7 and $La_{1.2}Mo_6S_6$ show θ_E terms (McMallum *et al.*, 1978).

Another group of new super conductors is the graphite intercalates. Investigations of the order–disorder transitions were made by Suematsu *et al.* (1979) on $C_{24}Rb$ and $C_{36}K$. Super conducting $RbHgC_8$ ($T_c=1.93$ K), $KHgC_8$($T_c=1.46$ K), etc were studied by Alexander *et al.* (1981). The data are consistent with the expected behaviour. The existence of Schottky anomalies in new super conducting C_8K, C_8Cs, C_8Rb, etc is also known (Alexander *et al.*, 1979). A decrease of θ_D is noticed when Hg is added to KC_8 and RbC_8 from 374 K to 260 K and 439 K to 238 K. This is consistent with the Hg compounds being super conducting (Alexander *et al.*, 1981). The order–disorder transitions in $C_{24}Rb$ are seen in C_p data and are confirmed to be due to the changes in Rb layer ordering (Suzuki *et al.*, 1981).

CALORIMETRY AT HIGH PRESSURES

The area of high pressure calorimetry has developed only in the last 10–15 years (Loriers-Susse, 1980, 1980a). Measurements are reported on systems of specific interest such as SmS, V_2O_5, NH_4Cl, etc and on many classes of materials (metals, polymers, etc) for generating thermodynamic data in the *PT* plane.

Measurements on SmS (Bader, Phillips and McWhan, 1973) were made to analyse valence fluctuations. SmS shows a transition at 298 K and 6.5 kbar with no change in crystal structure but an 8% volume change. SmS, SmB_6, α-Ce, etc show large linear term contributions to C_p at low temperatures. These are known to be due to the shifting of the f electrons from the valence band to the conduction band. The high pressure low temperature calorimetry has shown that the entropy of f levels in SmS disappears and confirms the valence fluctuations model. V_2O_3 has a metal insulator transition at 150–160 K and 1 atm. This is known to be suppressed by non-stoichiometry, doping or high pressure. On suppression, V_2O_3 has a large electronic contribution to C_p showing a system on the verge of localization. Measurement of C_p at 1 and 25 kbar and at 0.3–10 K have shown that the large linear term is integral to the sample and not due to dopants (McWhan *et al.*, 1973).

Bismuth is usually used for high pressure calibration. C_p measurements on Bi show that for the BiI, BiII and BiIV phases the $\theta_D(C_p) \sim \theta_D$ (elastic) (Dzhavadov, 1973). Measurements on Al and Ni (Bastide and Loriers-Susse, 1975) show that the total change in C_p is rather low (to 100 kbar, 4% for Ni and 11.4% for Al). Accurate ($\sim 2\%$) measurements have been reported on Ce up to 20 kbar at 300 K. At the γ–α phase transition, an expected sharp peak is noticed (Bastide *et al.*, 1978). An interesting example of high pressure calorimetry on metals is on Ga (Eichler, Bohm and Goy, 1980). GaI has a T_c of 1.08 K ($\theta_D = 325$ K and $\gamma = 0.6$ mJ/mol K^2); GaII is a super conductor with $T_c = 6.4$ K at 35 kbar. As expected, θ_D is 178 K and $\gamma = 1.75$ mJ/mol K^2. The changes in θ_D and γ are expected for an increase in T_c. Also $\theta_D(p)$ shows larger changes for GaI and this shows that the Debye harmonic model is a better model for GaII.

NH_4Cl has been an interesting candidate for high pressure calorimetry. At the phase transition in NH_4Cl, C_p changes by a factor of 30 to 40 at 1 atm but only by a factor of 2 at 3 Kbar (Amitin *et al.*, 1973). Measurements of C_p and λ at 140–520 K and $P \sim 20$ Kbar to study the phase transitions I–II–III were reported by Ross and Sandberg (1979). At the II–III phase transition, λ is continuous but $(d\lambda/dT)_p$ shows a sharp change. ρC_p shows a λ-type transition (*see Figure 15*). The exponents however could not be evaluated. The transition seems to be of the first order only up to 2 kbar. The phase II is a plastic crystal phase. A similar phase transition is the III–IV transition in furan (C_4H_4O). Here 4 phases are known. C_p measurements (Andersson, 1980) show that PI and PIV are plastic crystals and that the III–IV transition is of the second order. Plastic crystals are of interest as they show no resistance to molecular reorientation and plastic deformation. They have common features with liquid crystals but are less well studied (Daniels, Cladis and Keyes, 1980). An example which is well studied is C_6H_6. Three phases are known P–I (fcc) (279–186 K), P–II (monoclinic, < 186 K) and P–III (the high pressure phase). There is a possible triple point at 191 K and ~ 0.2 kbar. C_p and λ measurements have shown that for PI–II transition, $\Delta\rho C_p$ 12%, $\Delta\rho = 5\%$ and that $C_p\text{III} > C_p\text{II}$ (Andersson, 1978). The transition enthalpies are found to be: ΔH (I–II) (1 atm) $= 672 \pm 0.07$ kJ/mol; ΔH (II–III) (1.8 kbar) $= 1.723 \pm 0.003$ kJ/mol; and ΔH (III–I) (1.8 kbar) $= 5.98 \pm 0.02$ kJ/mol (Arntz, 1980). Several other measurements on hydrocarbons have also been reported (Nazeiv, Mustafaev and Abasov, 1979; Gerasimov and Grigorev, 1979; etc). Measurements are also reported on glycerol (Sandberg, Andersson and Backstrom, 1977), ethylene (Miyazaki, Hejmadi and Powers, 1980), propylene (Allen, Paulson and Wheatly, 1981), etc. Measurements on polymers such as polyacetylene, nylon, teflon etc, have shown that C_p changes are large compared to metals (*see Figure 16*) and also there is some decrease in (dC_p/dP) at higher pressures (Johnson and Miller, 1970; Engelu and Meisner, 1980; Belastotskii *et al.*, 1976; Andersson and Backstrom, 1973; Andersson and Sundquist, 1975; and Dzhavadov 1975).

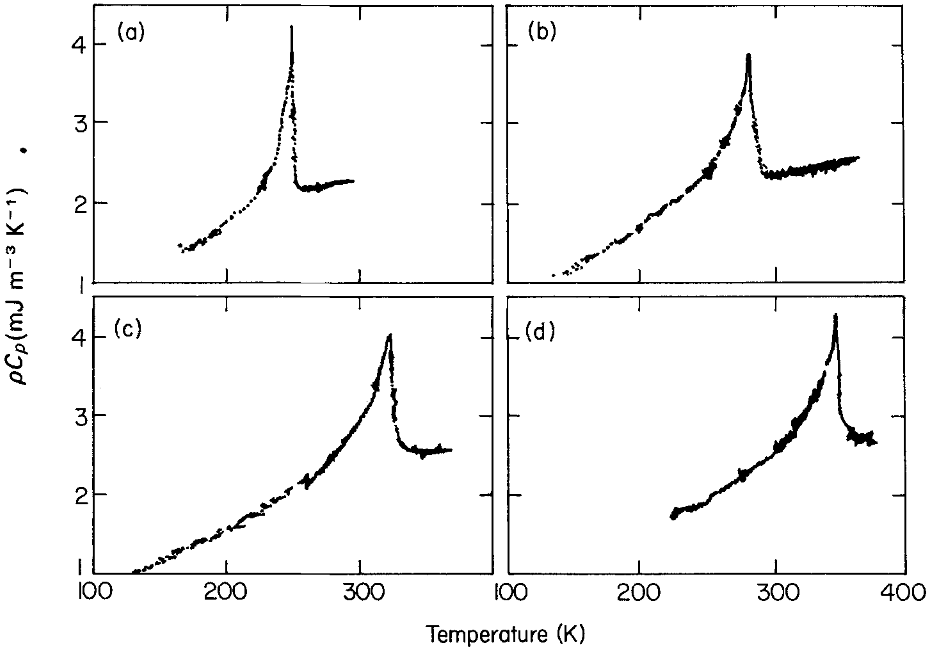

FIG. 15. Variation of ρC_p of NH_4Cl at the II–III transition. (a) 0.05 GPa, (b) 0.50 GPa, (c) 1.25 GPa and (d) 2.0 GPa (Ross and Sandberg, 1979).

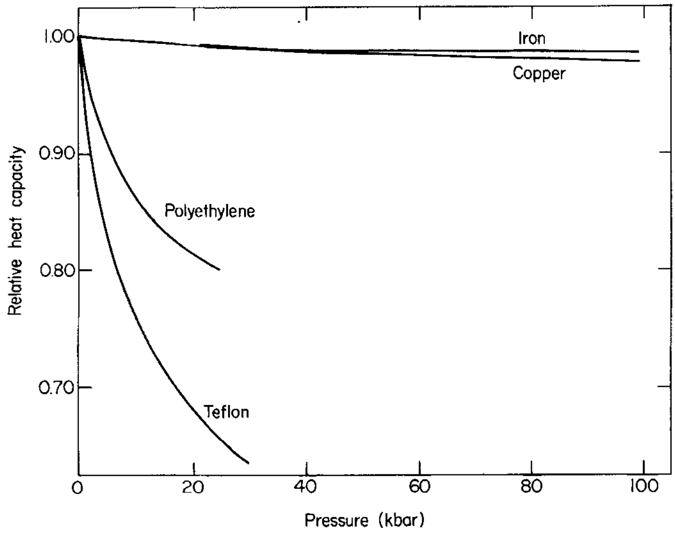

FIG. 16. Variation of heat capacities of some representative materials with pressure (Cezairliyan and Beckett, 1975).

CALORIMETRY OF THIN FILMS

Measurement of specific heats of thin films is of interest for several reasons. Thin films have an almost two-dimensional character. The surface to volume ratio is very large and it would be of interest to see if the surface contribution, normally expected to be a T^2 term at low temperatures, is present (Yates, 1972). While other aspects of thin film phenomena are well characterized (Chopra, 1969), C_p measurements are reported only for the thin film super conducting phases. Super conductivity in thin films, particularly amorphous films, is reviewed by Bergmann (1976). Measurements of C_p on Bi + 10% Sb films were made by Krauss and Buckel (1975), who report the absence of the C_p contribution from tunnelling states, but the accuracy is not good enough for confirmation. Measurement of C_p of In (+Sb) films showed that the lattice contribution, is increased by a factor of 3.5 in comparison to crystalline In. Also $\theta_D=61$ K compared to 110 K for bulk In (Comberg, Ewert and Wuhl, 1976). The Eliasberg function, α^2 ($f(\omega)$ is determined by C_p and tunnelling experiments. Similar measurements on amorphous Tl(+Te) films were also made (Wuhl, Comberg and Ewert, 1980). They also find that θ_D is 58 K compared to 78 K for bulk Tl. C_p increases by 3 to 10 orders of magnitude showing that there is a large change in phonon spectrum. The $\alpha^2F(W)$ determined for the films shows the characteristics of most amorphous films. *Figure 17* shows the $\alpha^2F(\omega)$ for the films compared to crystalline Tl. Similar results are reported for the Pb + Bi films (Kampf and Buckel, 1977). Interestingly, work on granular Al films by Greene *et al.* (1972) and by Filler, Lindefeld and Deutscher (1975) shows similar results. They also find an increase in C_p (lattice) and in the density of phonon states. T_c is also increased to 2 K and there is a 28% decrease in θ_D. The authors suggest the presence of soft phonon modes as the cause for the enhancement. Typical data on Al films is shown in *Figure 18*.

Recently, C_p measurements were reported on In films with magnetic impurities (Mn and Cr) (Gibson, Ginsberg and Tai, 1979). The impurity concentration is low enough for impurity–impurity interactions to be neglected. The authors determined ΔC_p, the change in C_p at T_c and show that $\Delta C_p/C_p(0)$ shows a rapid decrease when plotted against $T_c/T_c^{(0)}$($T_c^{(0)}$ and $C_p^{(0)}$ are for pure films). The Abrikosov and Shibas theories are compared. The former does not work well for 'd' impurities as for 'f' impurities. Similar

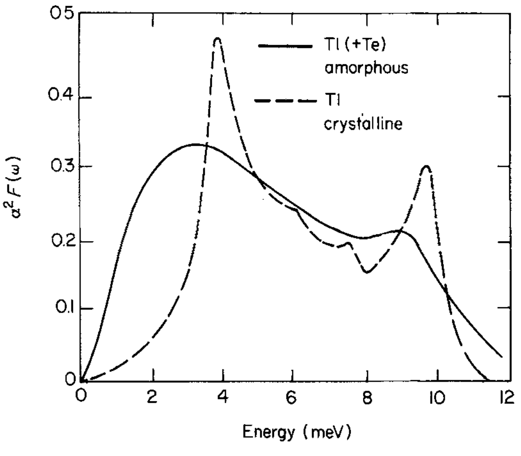

FIG. 17. Comparison of the Eliasberg function $\alpha^2F(\omega)$ for crystalline Te and amorphous Te thin films (Wuhl, Comberg and Ewert, 1980).

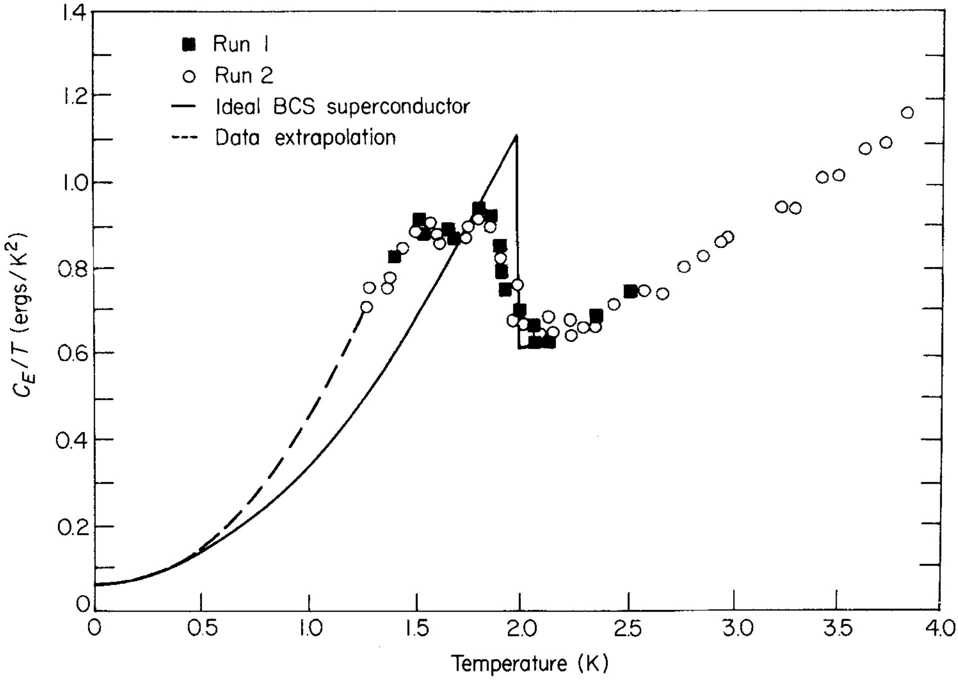

FIG. 18. Experimental heat capacity of Al film B8 in the super conducting transition region. The circles are from later measurements taken after the film was aged in air for 3 months at room temperature. The solid line represents the heat capacity of an ideal BCS super conductor with the same electronic heat-capacity coefficient as the sample and $T_c = 2.0$ K. The nonzero intercept at $T = 0$ is the result of non-super conducting addendum (Greene *et al.*, 1972).

work has been reported on Al–Mn, Zn–Cr and Mo–Fe films (Takayanagi and Sugawara, 1975).

A recent work by Gust, Predel and Stenzel (1979) offers an interesting example, wherein surface entropies and surface heat capacities were calculated for pure metals. ΔS_0^σ and ΔC_p^σ for Al and Ag are reported at 0 K and ~200 K. While they explicitly do not consider thin films, this work probably has interesting possibilities of application to thin films.

EQUILIBRIUM THERMODYNAMICS OF MATERIALS

Calorimetry is used extensively to study equilibrium phase and energy relationships of various materials. The literature in this is very large, but new and interesting examples come up even now.

Hume-Rothery phases are well known but detailed thermodynamic data are not yet available (Massalski and Mizutoni, 1978). As a part of a study of Hume-Rothery phases, C_p data on Cu–Ge, Ag–Sn, Au–Sb, Au–Pb and related systems were analysed in the 230–1000 K regime. The data for all the equilibrium phases and transition enthalpies have been determined only now (Wallbrecht, Blachnik and Mills, 1981, 1981a). The thermodynamics of fused salts of $Na(NO_3)$, $Ca(NO_3)_2$,

$K(NO_3)$, $Na_2Cr_2O_7$, $K_2Cr_2O_7$ and mixtures were studied as part of a programme to study the possibilities of these materials for energy storage (Dancy and Nguyen, 1980; Nguyen and Dancy, 1980). To study polymorphic transitions, Sn–Se alloys were investigated by Balde *et al.* (1981). The variation of C_p at polymorphic transitions is seen to be systematic (Gorecki, 1978). For HCP–FCC or HCP–BCC transitions, C_p decreases and for FCC–BCC transformation, C_p increases. These changes are regular, like changes in atomic volume. For work at cryogenic temperatures, C_p data on both construction materials and standards are of interest. Examples of recent work are on fibre reinforced materials (Collings and Smith, 1978), graphite (Rapp, DeSouza and Lerner, 1979), adsorbed gases (DeSouza, Rapp and Lerner, 1978), etc.

High temperature thermodynamics

These measurements are usually made by pulse techniques where very large power is used over very short time scales (Lakshmikumar and Gopal, 1982). They alone can provide very high temperature thermodynamic data. Examples are the measurements on graphite (1500–3000 K), $Nb_{80}Ta_{10}W_{10}$ alloy (1500–2800 K), $Hf_{97}Zr_3$ alloy (1500–2400 K), $Nb_{99}Zr_1$ alloy (1500–2700 K), etc. Here the major interest is in C_p data and calculation of G^0 or H^0. The results are shown in *Figure 19* (Cezairliyan and Righani, 1975; Cezairliyan, 1973, 1975, 1975a). Examples of other work are on SiC, and graphite (1300 K) (Naito *et al.*, 1979) and the study of (α–β) phase transition at 1166±7 K in Ti, $\Delta E = 4170$ J/mol^{-1} (Cezairliyan and Miller, 1978).

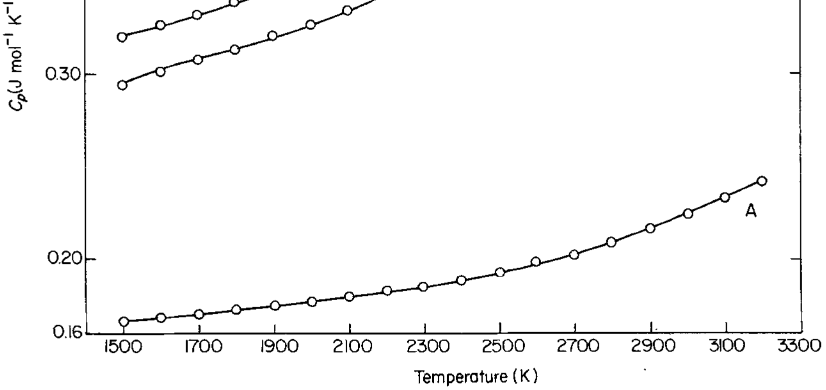

FIG. 19. The variation of specific heats of various refractory metallic alloys at high temperatures. (A) $Ta_{10}W_{90}$, (B) $Ta_{10}W_{10}Nb_{80}$, (C) $Nb_{99}Zr_{01}$ (Cezairliyan, 1973, 1975, 1975a).

Calorimetry of actinide and related materials

There are a large number of calorimetric measurements on actinide metals and compounds—in particular compounds of U, which are of interest for nuclear energy. The measurements on actinide metals are reviewed by Mortimer (1979). γ, ρ, $d\rho/dT$ and α (the expansivity) show maxima at Pu as one goes through the periodic table. Variations of θ_D are however random. αU, αPu and αAm show nuclear Schottky anomalies. Generally the difficulties in measurements on these materials are:

1. Toxic nature.
2. Radioactive self heating.
3. Difficulties in separating magnetic, lattice and Schottky contributions.

To avoid self heating, it may be necessary to redesign the experimental set up (Hall *et al.*, 1975; Fellers *et al.*, 1979). Measurements on a number of actinide compounds are reviewed by Blaise (1979).

UO_2, has a λ-type anomaly at 30.44 K (T_N). The excess C_p at 30–120 K is said to arise from Jahn-Teller interactions. UO_2 has a CaF_2 structure. In an interesting study of UO_2, Long *et al.* (1980) used C_p data on UO_2 to calculate vapour pressure of UO_2 up to 2150 K. The data are then used to study hypothetical accidents in nuclear reactors. NpO_2 which is also of CaF_2 structure shows a peak in C_p at 25 K which is not yet understood. Monoclinic UF_4 has a Schottky anomaly at 6.4 K; U has two sites, which couple to the electric field causing the anomaly. UI_3 has $T_N = 3.4$ K and a λ-type C_p behaviour. This system belongs to the 2d Ising model and has interestingly significant SRO even at 4.2 K (Blaise, 1979). In UC, all 5f electrons are delocalized, resulting in a high γ value (20 mJ/mol K^2). Antiferromagnetic UN ($T_N = 52$ K) and PuN also have high γ values. Other actinide compounds which are well studied are US and UP (Westrum *et al.*, 1968; Takahashi, 1974). UP has a phase transformation at 121 K, US has a transformation at 180.1 K ($\Delta S = 1.6 \pm 0.2$ cal/mol K; $\Delta H = 2.31 \pm 0.20$ cal/mol (*see Figure 20*).

Calorimetry of rare earths

Calorimetric investigations on rare earth materials are very popular and are well reviewed (Craig, Wallace and Smith, 1979; Sundstrom, 1978). The metallic materials show complex behaviour, for C_M, and the nuclear spin interacts with the 4f quadrupole field gradient and causes nuclear Schottky anomalies at low temperatures. Generally, the γ values are large but a part of the problem is the separation of C_M and C_L. The C_p data of RE alloys with Fe are recently reported (Germano, Butera and Gschneider, 1981). Alloys of the formula RFe_2 (R = Gd, Tb, Dy, Ha, Er, Tm and Lu) were investigated. The values of $(G^0_{298} - H^0_0)$ were determined. The values show a maximum at $HoFe_2$ due to magnetic contribution. The Laves phases $GdFe_2$, $ErFe_2$ and $LuFe_2$ surprisingly show $C_M = 0$ at $T < 8$K. Data on rare earth oxides are reviewed by Nguyen (1980).

Calorimetric study of Guinier-Preston zones

The process of precipitation and age hardening in Al alloys can be studied by x-rays, resistivity and electron microscopic studies. Calorimetry is now used to assist these. Precipitation in Al–Zn–Mg alloys proceeds by the formation of metastable phases and the heat evolved can be measured. The dissolution and transformation in these phases

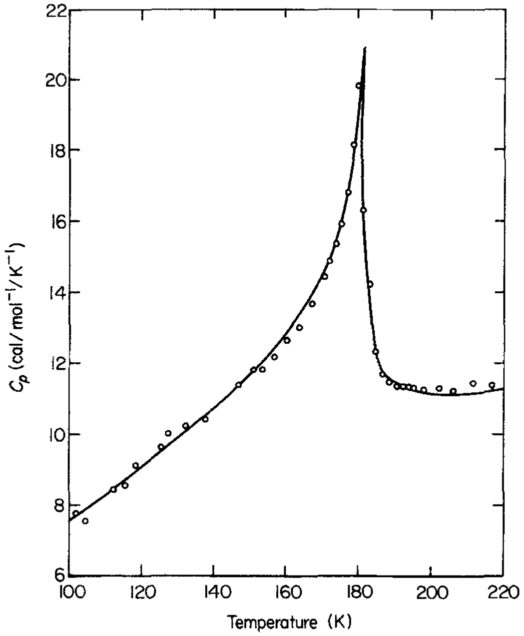

FIG. 20. Heat capacity anomaly of $US_{1.00}$ (pellet, 3.7671 g) (Takahashi, 1974).

can be studied (Hirano, 1974; Nozato, 1980; Lucern *et al.*, 1980). In the 20–200 °C range, G.P. zones and metastable phases are noticed. The metastable products nucleate on G.P. zones or vacancy clusters formed by quenching. The following transformations are noted in this process. Supersaturated solid solution → spherical G.P. zones → internally ordered G.P. zones → metastable M phase + $MgZn_2$ → Al_3Mg_3Zn + equilibrium phase.

One-dimensional materials

The theoretical interest in the physics of one dimension, especially the possibilities of new types of phase transitions including excitonic super conductivity have made this area active (Andre, Bieber and Gautier, 1976; Miller and Epstein, 1976). Calorimetric work has not been very popular because the crystals are small and experiments are very difficult. However, using the modern methods, θ_D has been evaluated for MNP–TCNQ, Q–$(TCNQ)_2$ with pellet samples. Direct evidence for phase transitions in TTF–TCNQ was obtained by a.c. calorimetry (Craven *et al.*, 1974). Phase transitions at 52.6, 49, 48, 46 and 37 K were detected by the relaxation method (Djurek *et al.*, 1977). These results are shown in *Figure 21*. These are all caused by the softening of specific modes in the quasi one-dimensional lattice. The C_p measurements on I_2 doped $(CH)_n$ show that $C_p = AT$ and that though doping with I_2 changes the σ by a large amount, C_p is not effected, probably indicating that I_2 is not entering into the structure (Mermilliod, Zuppiroli and Francois, 1980).

Ferroelectrics at low temperatures

The low temperature C_p measurements on ferroelectric and related materials such as

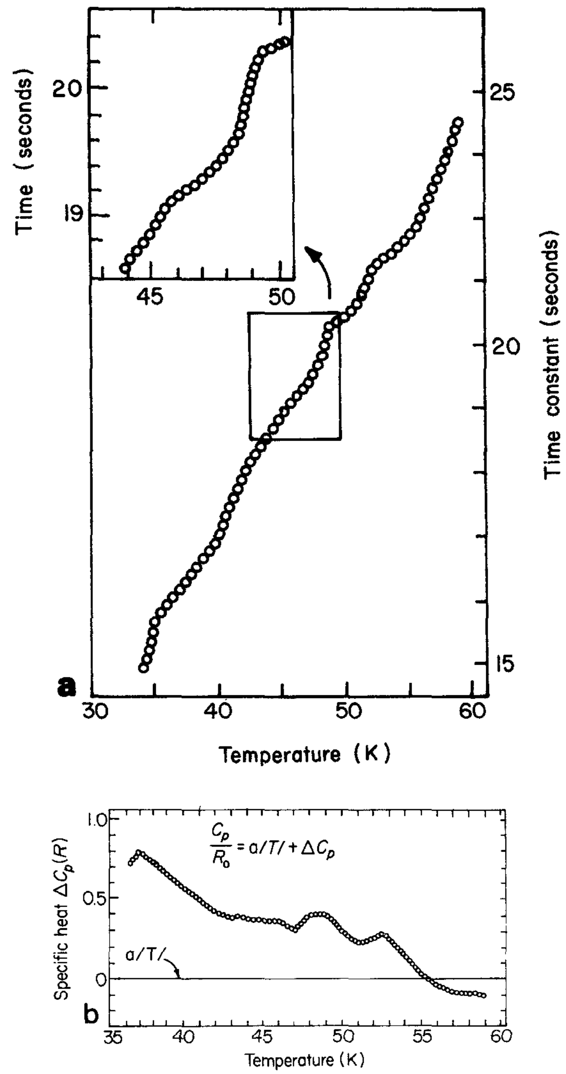

FIG. 21. (a) The temperature dependence of the time constant for TTF–TCNQ and (b) is the curve from which the linear contribution was deduced. Specific-heat data related to the four phase transitions in TTF–TCNQ. Because of undefined background, an arbitrarily chosen linear contribution $a(T)/R_0 = 0.115T + 6$ was subtracted from the specific heat (Djurek *et al.*, 1977).

PbF_2, $KTaO_3$, $BaTiO_3$, KDP, TGS, $LiNbO_3$, PZT, $Pb_2Nb_2O_7$, etc have shown that C_p is generally given as

$$C_p = AT^3 + BT^{3/2} + C(\theta_E)$$

The T^3 term is the lattice contribution, in addition to which a contribution from a single Einstein frequency

$$\nu_E = \frac{h\theta_E}{K}$$

is found. ν_E corresponds to some soft vibrational mode observed in spectroscopic studies. For example in TlCl, $\nu_E = 89\ \text{cm}^{-1}$ and for $BaTiO_3$, $\nu_E = 99\ \text{cm}^{-1}$. The $T^{3/2}$ term corresponds to domain wall movement (Lawless, 1976, 1980). Schottky anomalies were noted in $PbNO_3$ and $CdNbO_3$ with $\Delta T \sim 50$–70 mK due to interaction of the Nb^{5+} quadrupole moment with electric field gradients. The influence of electric fields on C_p data was also noticed (Lawless, 1980; Ramos, Delicerro and Zamora, 1980).

The most significant observation is the identification of a single dominant acoustic phonon as that which governs the low temperature C_p for all ferroelectrics. This analysis however is questionable (Burns, 1980). He showed that excess C_p need not be attributed to ν_E but may be explained on the basis of a realistic phonon spectrum and a corresponding variation of θ_D as discussed for other materials (Gopal, 1966). In addition to the physical picture, which is important, the above discussion shows the complexity involved in analysing C_p data and separating individual contributions.

Polymeric materials

Calorimetry has been widely used for studies on polymers, in particular glassy polymers. Measurements on vapour deposited and liquid quenched Se have shown that annealing of vapour deposited Se is needed to get C_p and IR data similar to bulk glassy Se giving insight into short range order of glasses (Stephans, 1978). C_p measurements near T_g for polymers are very important as T_g is in these systems related to the free energy and hence C_p (Aleman, 1980). However, it is known that ΔC_p, change in C_p at T_g or ΔS_g or T_g/T_2 (T_2 is the temperature at which ΔS of super cooled liquid over crystal is zero) are not constant for all polymers. Empirically,

$$\frac{\Delta S_g}{\Delta S_m} = M \exp N^2 Y^2$$

Here

$$Y = \frac{T_2}{T_g} - \frac{T_2}{T_M}$$

and $N^2 = 12$ for polymers and 14 for non-polymers (Privalko, 1980). In addition to empirical results, attempts at a thermodynamic theory for glassy polymers are made (Kovac, 1981).

The discontinuous change in C_p at T_g for polymers is shown to be consistent with the Gibbs-DeMarzio model for glass transition (Gibbs and DeMarzio 1958; DeMarzio and Dowell, 1979). One can also mention that C_p measurements on glasses (non-polymeric) by Turnbull were the first to suggest that the ideal glass transition may be of second order (Turnbull, 1969; Angell and Sichina, 1976). The relaxation of polymeric materials due to annealing and consequent changes in H and C_p are also studied (Ott, 1979; Lagasse, 1980). We have considered only a few examples. More detailed analysis is available in recent monographs (Fava, 1980).

Metallic glasses

The measurement of C_p of metallic glasses particularly at low temperatures is of extreme interest (Onn, 1981). There are contributions from lattice electrons and in ferromagnetic materials from magnetic ordering. The electronic contribution $C_E = \gamma T$ but γ is much larger than expected from the known density of tunnelling states. The

$\theta_D(T)$ has been determined for many ferromagnetic glasses and shows a minimum at about 10–50 K (Onn, Sundermier and Krause, 1981). This behaviour is of course well known in crystals (Gopal, 1966). Interestingly some compositions, for example PdCuSi alloy, show an excess Einstein contribution (Chen and Haemmerle, 1972). The variation of γ with the metal and metalloid concentration, shows that a split band model is to be used for the electronic states (Onn, 1981). The magnetic contribution, to C_p, is a constant for incipient ferromagnets such as $Ni_{80}P_{12}B_8$ and $Ni_{78}P_{14}B_8$. In spin glasses, $C_M \sim AT$ for $T < T_s/2$ where T_s is the spin glass transition temperature. Examples are FeNiPB glasses with 7–8% Fe. In ferromagnets, $C_M \sim T^{3/2}$ but in most samples, C_M is only 5% of C_p and once again separating C_M is difficult. Recently, a quasi-equilibrium behaviour of reproducibility in physical properties of annealed metallic glasses has been noted (Scott, 1981). It is seen that relaxation and annealing affect $\theta_D(T)$ and $\theta_D(0)$ but the complete analysis is not available. Representative numerical values for the Metglass 2826 and 2826A are (Phillips and Stewart, 1978):

$$\gamma = 1.78 \times 10^{-4}\ \mathrm{J/gK^2} \quad \theta_D = 130\ \mathrm{K} \quad 2826$$
$$\gamma = 2.86 \times 10^{-4}\ \mathrm{J/gK^2} \quad \theta_D = 110\ \mathrm{K} \quad 2826\mathrm{A}$$

Spin glasses

Spin glasses, as the name implies, have spins frozen in random directions below the transition temperature. The field is extensive and reviews of theoretical and experimental areas are available (Mydosh, 1978; Levy and Hesegawa, 1977). The mean field theories such as the Anderson-Edwards model correctly predict a cusp in magnetic susceptibility at T_{sg}. They however predict a cusp for C_p while experiments show a broad maximum for example in MnSi, MnGe, $MnGe_2$ (Hauser and Hsu, 1981). Fagle *et al.* (1981) made accurate C_p measurements (0.01% error). They find that C_p is continuous at T_{sg}, (dC_p/dT) shows a broad maximum over ± 2 K at T_{sg}. C_p data in presence of magnetic fields exhibits $C_p/T = A + BH^2$, where B is temperature-dependent and has a minimum at T_{sg}. The absence of expected behaviour is linked to the non-ergodicity of the system. The main features are seen in *Figure 22*. Another interesting but as yet unexplained feature is the power law behaviour at very low temperatures. For example $C_p \sim T^{1.6}$ at very low temperatures in Sc, 2.9 Gd (Condron *et al.*, 1981; Levesque, Condron and Costa, 1980).

MEDICAL AND BIOLOGICAL APPLICATIONS OF CALORIMETRY

These are relatively new areas of calorimetric work. The extension of thermal studies to biochemical reactions is fairly straightforward but we discuss, mainly, applications of specific heat measurements. In recent years, this area has been very active and a number of reviews are available (Riyaldi and Biltonen, 1975; Lamprecht and Schaarschmidt, 1977; Williams, 1977; Barisar and Gill, 1978; Martin and Narini, 1979; Spink, 1980). The experimental methods generally used are the DSC, the Tian-Calvet micro-calorimeter and their modifications. A completely new system developed is the 'whole body calorimeter' (Jecqueir, 1977; Lakshmikumar and Gopal, 1982) used to study biochemical energy conversion of whole specimens.

Calorimetry of biopolymer solutions

The use of calorimetry to investigations on biopolymer solutions is reviewed by

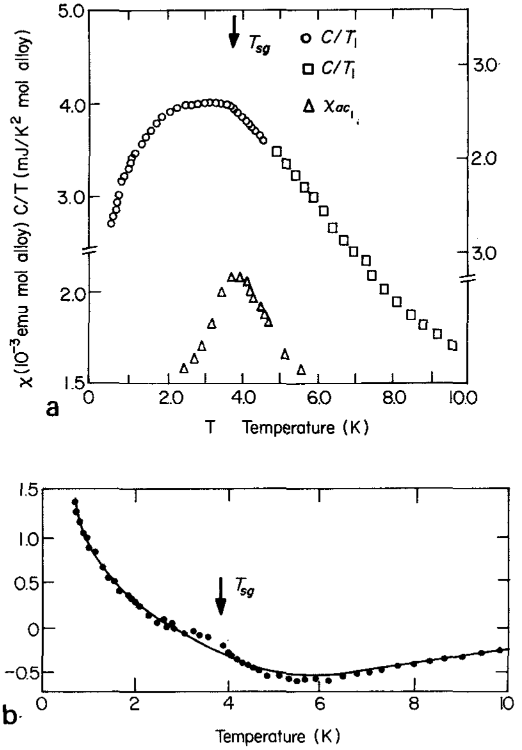

FIG. 22. Variation of C_p and χ of a spin glass at T_{sg} (Fagle *et al.*, 1981).

Andronikashvili *et al.* (1979). They define four major areas of work as shown in *Figure 23.*

1. 273–400 K. In this regime, conformation changes in aqueous solutions of proteins, nucleic acids, etc are studied and thermodynamic parameters of the adsorption processes are evaluated.
2. 273–230 K. Here, ice-water phase transitions, in the presence of biopolymers, are investigated and information regarding hydration of biomolecules is obtained.
3. 250–210 K. The ligand binding of biopolymers is investigated by studying ice-biopolymer-salt solution eutectics.
4. Low temperatures. Here thermodynamic parameters of biopolymers in various conformations are obtained. Specific examples of these areas are discussed by various authors (Privalov, 1974; Daures, Delhas and Dupart, 1975; Andronikashvili and Mrevlishville, 1976).

Transformation and interactions of biopolymers

The interactions of enzymes and substrates, metal ions and ligands are examples of interactions studied by calorimetry (Barisar and Gill, 1978; Riyaldi and Biltonen, 1975). The work of Belaich and Sari (1973) is a typical example. The formation of complexes of ATP, ADP and AMP with Mg^+ is investigated and ΔF, ΔH and ΔS values are determined. It is seen that the entropy factor is the driving force for complex

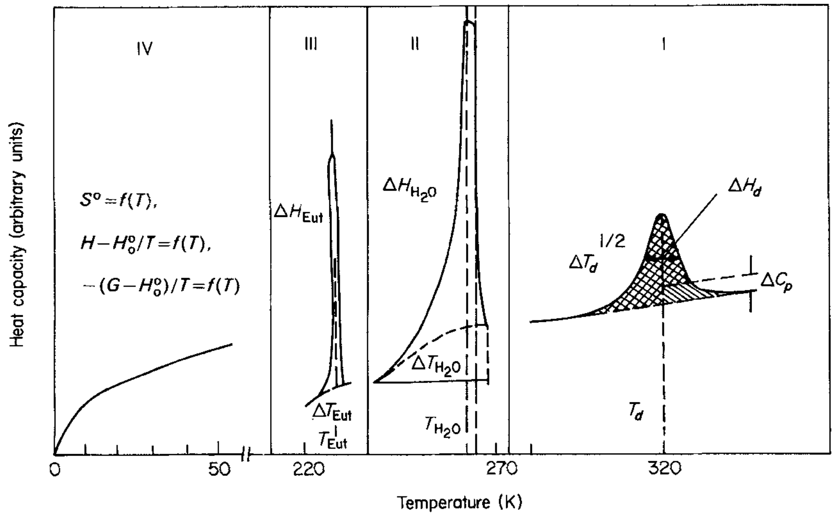

FIG. 23. The four regimes of calorimetry of bipolymer solutions (Andronikashvili *et al.*, 1979).

formation and that the stability of the complex seems to increase with the length of the phosphate chain.

The interactions of proteins, DNA, etc have also been studied using calorimetric methods. The endothermic transitions involved were studied by Williams *et al.* (1979). Transformations in macromolecules can also be studied (Wyman, Gill and Colosimo, 1979). The thermal transitions are analysed as due to allosteric phenomena and are understood on the basis of ligand bonding. This explains the melting of nucleic acids, reversible heat of denaturation of proteins etc. Studies on RNA show that the total internal energy decreases when the nucleic acid reacts with the coat protein (Hinz, Srinivasan and Jaspaur, 1979).

The stability of collagen of various species was determined and the ΔS and ΔH values for disruption were determined by Privalov, Tiktopulo and Tischenko (1979). They showed that ΔS and ΔH values depend on total propyl and hydroxypropyl content and not on the number of stable H_2 bonds. An increase in amino acid content increases ΔG of microfolding and determines the mobility. The authors find a correlation between the stability of collagen and the physiological temperature of the species. A definitive level of mobility of collagen for efficient functioning of each living system is also seen.

Calorimetry as a clinical tool

Calorimetry is now a possible tool for clinical investigations. It is reported that calorimetry can be used in a study of plasma coaggulation, detection and identification of microbial activity and antibiotic action on microbes (Levin, 1973; Binford, Binford and Adler, 1973; Lamprecht and Shaarschmidt, 1977). The heat produced in a liquid culture by bacterial growth has a specific time evolution and this is sufficient to identify bacteria (Boling and Blanchard, 1973; Prosen *et al.*, 1974). An example is shown in *Figure 24.*

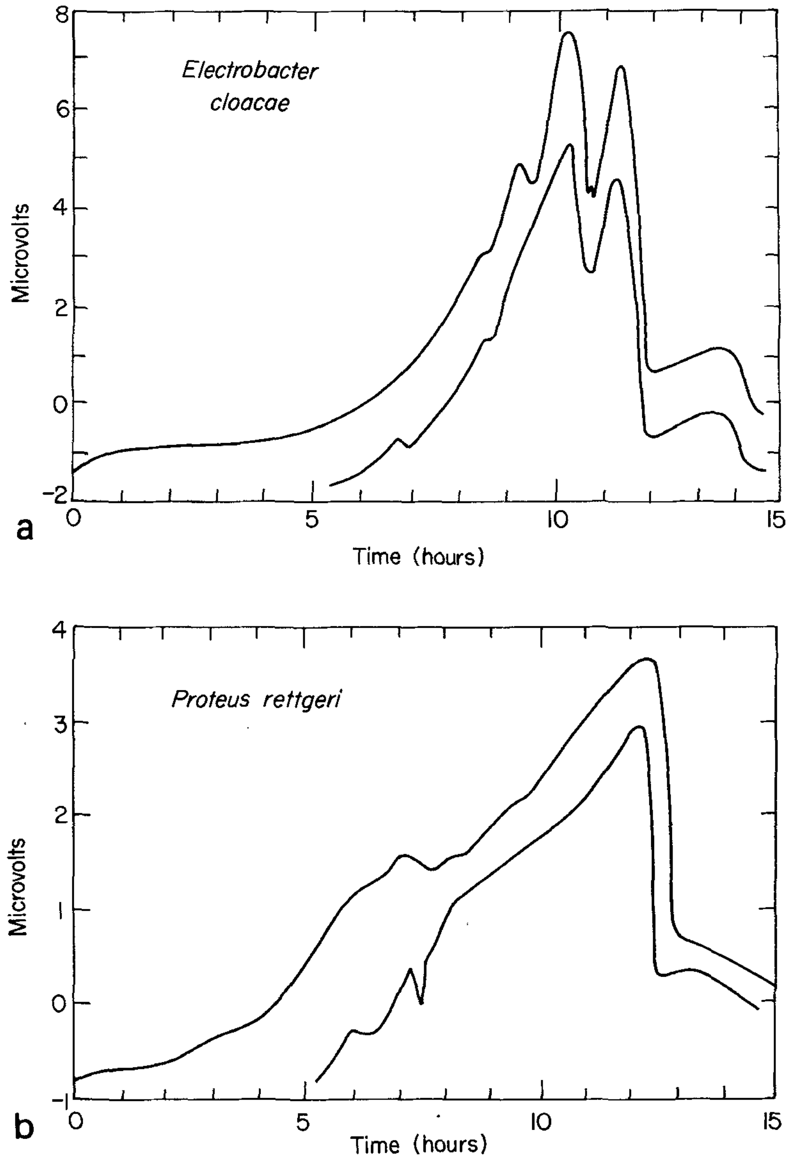

FIG. 24. The time evolution of heat due to two different bacteria indicating the use of this for identification. In each case two runs are shown to indicate repeatability (Prosen *et al.*, 1974).

In biological clinical assay, the substances of interest are to be identified in the presence of a fluid of variable composition. Prosen *et al.* (1974) have used blood serum as a test case. They studied the oxidase catalysed oxidation of glucose followed by catalase catalysed reduction of the product and found ΔH as -197 and -100 kJ/mol respectively. They also studied a biological process, the hexokinase catalysed phosphorylation reaction. The heat of the reaction is seen to be directly proportional to

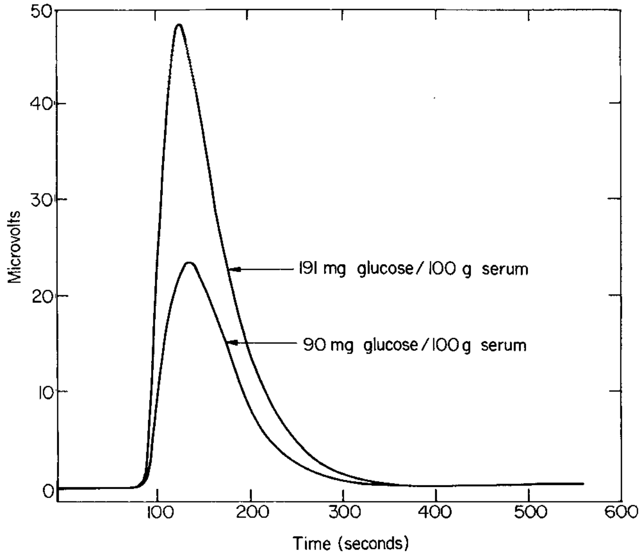

FIG. 25. Chart of calorimeter response for hexokinase catalysed phosphorylation of glucose in human blood serum. Two curves representing different concentrations of glucose are shown (Prosen *et al.*, 1974).

glucose content in serum and blood plasma (*Figure 25*) thus establishing the viability of calorimetric assays.

ACKNOWLEDGEMENTS

We acknowledge the help and assistance of Professor C. N. R. Rao, FRS and our colleagues in the laboratory in the preparation of the article. The financial support from the DST through the NTPP Project and the projects in the Department of Physics is also acknowledged.

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