BEHAVIOUR OF SPECIFIC HEAT C_p THERMAL EXPANSION β & COMPRESSIBILITY k_T NEAR MAGNETIC TRANSITIONS

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ABSTRACT

The Ehrenfest relations for second order phase transitions are shown to be unsuitable near ferromagnetic/antiferromagnetic-to-paramagnetic transitions, which show logarithmic or other infinities in specific heats. The applicability of the more general Pippard relations in such cases is investigated. C_p and β of Gd, Ni (ferromagnets) and MnF_2, MnO, MnTe (antiferromagnets) below the transition T_c are correlated well with the change of T_c with pressure. For chromium, k_T and β below T_c are also related to the pressure derivative of T_c. The effect of specimen purity is noticed in few cases. The Pippard scheme is free from the deficiencies of the Ehrenfest relations when correlating C_p, β and k_T near λ-transitions.

INTRODUCTION

Over years thermodynamic data near transition temperatures in magnetic materials have been collected in order to understand the details of the transition. The conventional method of correlating the observed anomalies in the various thermal properties in the vicinity of Curie or Neel temperature employs Ehrenfest's relations for second order phase transformations. These relations are derived from the considerations of equilibrium among the phases along the segments of S and V curves[15], if it is assumed that specific heats etc., change discontinuously across the transition and that there is no latent heat or volume change. For then

$$\frac{\partial X_1}{\partial P}\,\delta P+\frac{\partial X_1}{\partial T}\,\delta T=\frac{\partial X_2}{\partial P}\,\delta P+\frac{\partial X_2}{\partial T}\,\delta T;\; X=S \text{ or } V, \tag{1}$$

and one gets the Ehrenfest relations

$$\frac{DP}{DT}=\frac{1}{TV}\,\frac{C_{p1}-C_{p2}}{\beta_1-\beta_2}=\frac{\beta_1-\beta_2}{k_{T1}-k_{T2}}, \tag{2}$$

where C_p, β and k_T are respectively the specific heat at constant pressure, coefficient of cubical expansion and the isothermal compressibility, (DT/DP) is the slope of equilibrium curve, *i.e.*, the change in transition temperature with pressure and the suffixes 1 and 2 refer to the two phases in equilibrium. Such a correlation has been attempted by a number of authors.[27, 17, 1]

COMPARISON OF EHRENFEST AND PIPPARD SCHEMES

However, in the last few years, careful, high resolution studies on specific heats and thermal expansion of many substances suggest logarithmic and other infinities in the vicinity of transition point. For instance, logarithmic singularities have been found in the specific heats of $NiCl_2{\cdot}6H_2O$[39] $CoCl_2{\cdot}6H_2O$[43], $CoCl_2{,}2H_2O$[41], MnF_2[47], gadolinium[51], $CuK_2Cl_4.2H_2O$ and two cobalt salts[26], iron[23] and nickel[22(a)]. This renders an expansion as in eq·(1) invalid because the terms become infinite. Thus eq.(2) becomes indeterminate of the form $(\infty_1 - \infty_2)/(\infty_3 - \infty_4)$.

Further, the specification of the "jump" or discontinuity in specific heat or thermal expansion across the transition, as used by the early authors, becomes highly unsatisfactory in light of these recent measurements. To clarify this point consider the specific heat at zero magnetic field of an ordinary (type I) superconductor (figure I*a*). Experiments to within 10^{-5}°K[8] have shown that the specific heats are finite on both sides of T_c and that there is an abrupt discontinuity in C_p. Above T_c there is no "tail" in the specific heat curve and the system shows no indication of the change in property below T_c. The behaviour of thermal expansion, latent heat and compressibility confirm the superconducting transition at zero field as a truly second order phase change in the Ehrenfest sense. On the other hand the specific heat near a typical order-disorder transition has the shape shown in figure 1*b*. Recently many high precision studies, as mentioned earlier, have shown the specific heat to tend to infinity from both above and below T_c Crude experiments of insufficient resolution had earlier given finite peaks for the same materials and the excess specific heat over the normal smooth behaviour (shown by broken lines in figure 1*b*) had been taken as the "jump" in C_p. The excess specific heat is a measure of configurational ordering which persists a little above T_λ also as the "tail" in specific heat. These "jumps" will have to be taken as infinite according to the recent measurements. Indeed the helium I – helium II transition, which was the historic starting point of the Ehrenfest scheme, has now turned out to be different. The classic experiments of Buckingham, Fairbank and Kellers[7] in 1957 to within 10^{-6}°K of T_λ have shown C_p to tend to infinity as $\log|T - T_\lambda|$. Thermal expansion also shows a similar logarithmic infinity. Therefore the earlier calculation of DP/DT using finite "jumps", such as for instance given in the well known text of Roberts[37], cannot be given any weightage and the agreement with the experimental values of DP/DT must be largely fortuitous. Of course, if the approach to infinity were similar on both sides of T_λ, then

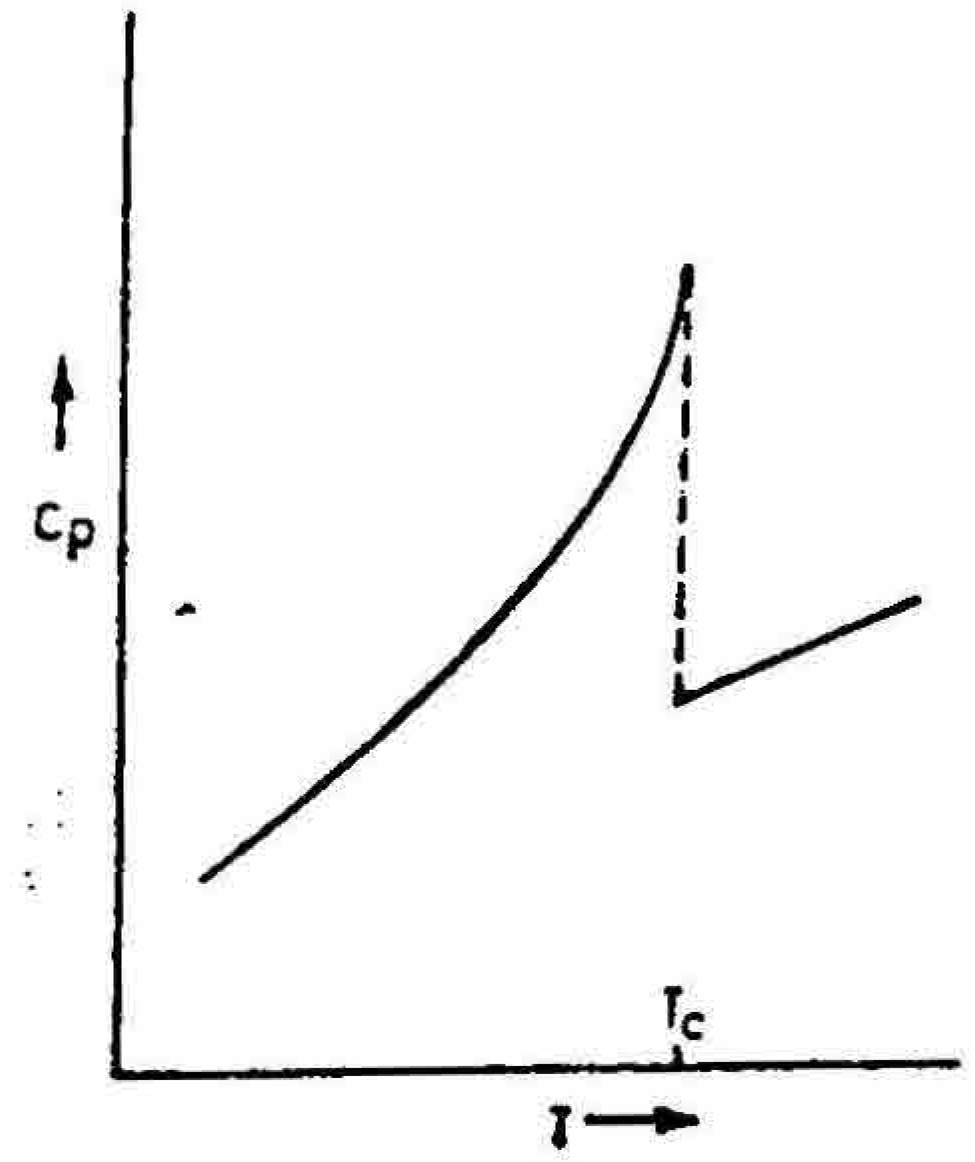

FIG I (*a*)

Specific heat at zero magnetic field of (type I) superconductor, the unequivocally proved case of an Ehrenfest second order phase change

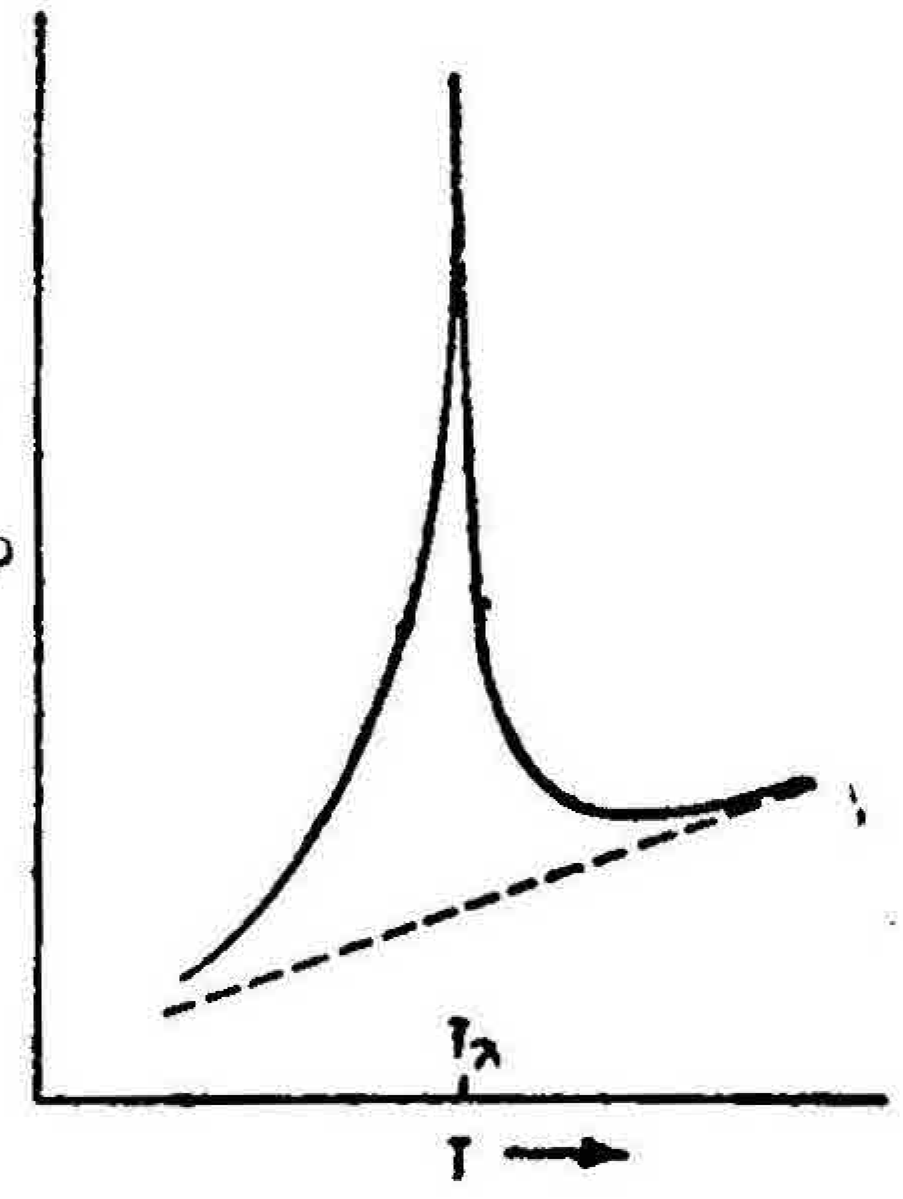

FIG. I (*b*)

Specific heat near a λ-type transition. The portion above the broken line is the configurational specific heat

one can still conceive of a "difference" $C_{p1} - C_{p2}$ for a given value of $|T - T_\lambda|$. This difference would be a definite constant for a range of $|T - T_\lambda|$ near T_λ. This situation occurs in helium where however such differences are very much smaller than the peaks of configurational specific heats. All the same in other λ-transitions, studies show that while the behaviour below T_λ is a logarithmic singularity, the behaviour above T_λ may be either a logarithmic singularity or a power law infinity. Therefore differences $C_{p1} - C_{p2}$ will depend upon the magnitude of $|T - T_\lambda|$.

The specific heats which must be used in the Ehrenfest relations (eq 2) are the limiting values as $T \to T_\lambda - 0$ and $T \to T_\lambda + 0$. The same is the situation for β and k_T. These limits are not the same as the magnitudes of the configurational peaks observed experimentally. The main objection to the use of Ehrenfest relations is that these limits as $T \to T_\lambda \pm 0$ are either infinite or very difficult to obtain in practice.

Under these circumstances it is necessary to correlate the thermodynamic quantities using a more general formulation, such as the Pippard relations[35, 36, 7].

Starting from the thermodynamic identity

$$-(\partial V/\partial T)_P = (\partial S/\partial P)_T = (\partial S/\partial P)_\lambda - (\partial S/\partial T)_P\,(DT/DP)_\lambda,$$

it follows that

$$C_p = TV\beta\,(DP/DT)_\lambda + c_o\,;\;\; c_o = T(DS/DT)_\lambda\,. \qquad [3]$$

Similarly starting from the identity

$$(\partial V/\partial P)_T = (\partial V/\partial P)_\lambda - (\partial V/\partial T)_P (DT/DP)_\lambda ,$$

it follows that

$$\beta = k_T (DP/DT) + \beta_0 ; \ \beta_0 = V^{-1} (DV/DT)_\lambda . \qquad [4]$$

In ordinary phase transitions the quantities c_o and β_0 show temperature variations which are not negligible compared to the variation of C_p and β near T_c. But in λ-type transitions C_p and β show very large variations and go nearly infinite at T_λ. For such cases c_o and β_o may be considered as "constants" near T_λ and this is the clyindrical approximation introduced by Pippard Equations (3) and (4) are the Pippard relations and are particularly suited to the cases where C_p, β and k_T show very large values.

The general Pippard relations include the Ehrenfest relations (2) as special cases. If the two phase have finite limiting values of β, C_p and k_T, then by taking the difference between the two phases equations (2) follow from (3) and (4). Pippard relations are more general and hold good even if β, C_p and k_T reach infinite values. Then the plots of C_p *vs*. β and k_T *vs* β reach asymptotic slopes determined by (DP/DT), as was beautifully exhibited in the λ-transition of helium-4. Apart from this case, the relations have been applied to λ-transitions in NH_4Cl, quartz etc.[15], but there has been no discussion of magnetic transitions in this framework.

In the present communication, an analysis of thermodynamic behaviour near ferromagnetic-paramagnetic and antiferromagnetic-paramagnetic transitions is made in the framework of Pippard relations. A summary of the results for antiferromagnetic MnF_2 and chromium was presented at the 10th International Conference on Low Temperature Physics, Moscow, 1966[12]. In a forthcoming note the ferroelectric transitions will be critically studied.

RESULTS FOR FEROMAGNETIC TRANSITIONS

The values of specific heats near the Curie point and DT/DP are available for a number of ferromagnetic materials including Fe, Co, Ni, Gd and Dy. However suitable volume expansion co-efficients near T_c are available only for Gd and Ni. In the case of Dy and Ho, the available data on expansivity[13] cannot be directly used for evaluation of the thermal expansion coefficient in the vicinity of Curie temperature. The thermal expansion curve of iron[30] shows an anomalous contribution in the region of ferromagnetic transition temperature, but the resolution is not sufficient to be used in the Pippard relations. The Pippard relation (*eq*. 3) was therefore tested out using the data for gadolinium and nickel.

GADOLINIUM

The ferromagnetic Curie temperature of Gd is about 291°K. Trombe and Foex[52] experimentally determined the thermal expansivity of Gd in the region of transition temperature. The negative sign of β near T_c was found to be consistent with the depression in Curie temperature with pressure, as observed by Patrick[32]. A number of later investigations on β using dilatometric methods[2, 4, 52, 10, 50] and X-ray lattice parameter measurements[9] have confirmed negative sign of β in the neighbourhood of T_c.

For estimating DT/DP of Gd using Pippard relations, the thermal expansion values were taken from the smoothed curves of Ergin[10]. The specific heats were taken from the work of Griffel et al.[18], who made measurements on the samples of 99·4 – 99·5 at % purity (Gd_x), and from the work of Voronel and coworkers[51], who made measurements on two samples of 99·3 – 99·7 at % purity (Gd_{27}) and 98·5 – 99 at % purity (Gd_{12}). The labels for identifying these samples are as given in the work of these workers. Since it is known that the exact value of T_c depends amongst other things, on purity of the substance, the values, reported in literature, differ by a few degrees. Therefore in obtaining the plots of C_p as a function of β below the Curie temperature, values of these functions were taken for same $(T_c - T)$ which are also indicated in the plots.

The plots of C_p as a function of volume thermal expansion are shown in figure II. It is seen from these plots that for the samples of high purity the points fall on straight line and for large $(T_c - T)$ departures from linearity are observed. In the case of sample Gd_{12} having a comparatively large impurity content the plot becomes erratic, though the indication of a thermal anomaly are certainly present. The values of DT/DP obtained from the slopes of these plots for the two samples are – 1·67°C/kbar (Gd_x) and – 1.75°C/kbar (Gd_{27}). These values, which have an error of about 10% on account of the error in locating the asymptotes in figure II, compare well with the values obtained from the measurements of magnetic permeability as a function of temperature at different pressures – 1·2°C/kbar[32], – 1.55°C/kbar[5], – 1·6°C/kbar[40] and – 1·34°C/kbar[25].

NICKEL

The measurements of specific heats near transition temperature (631°K) have been made by several workers on samples of high purity[46, 22, 55, 33] Williams[54] and Nix and MacNair[30] have measured coefficients of thermal expansion of nickel. X-ray investigations of β of nickel[34] also show a thermal anomaly in this region, but the resolution is not sufficiently good.

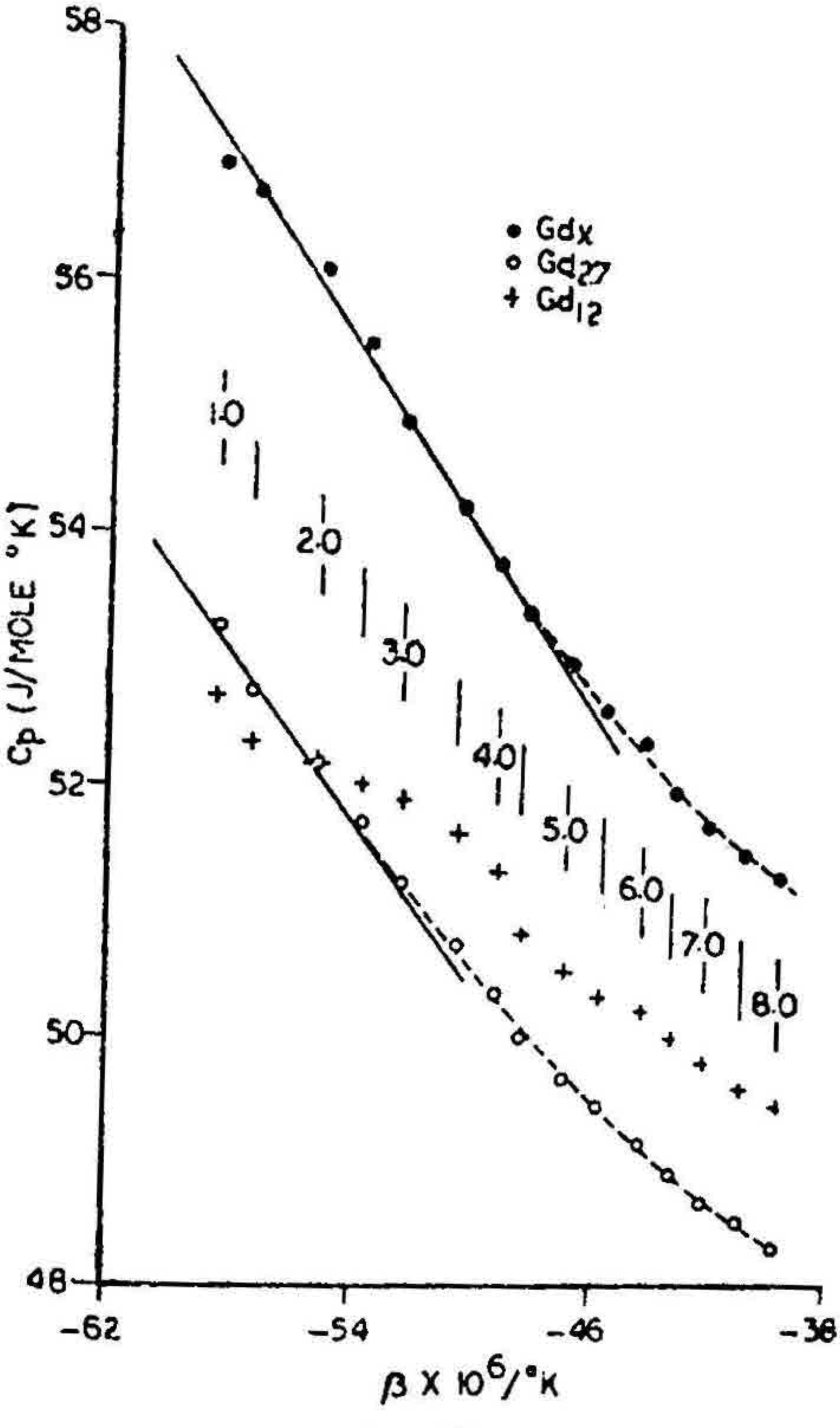

FIG. II

C_p of three samples of gadolinium as a function of β. The common values of $|T_c - T|$ in °K are indicated near the corresponding short vertical lines.

The specific heat measurements and thermal expansion curves on samples of different purity of nickel again show a dependence of thermal anomaly on the sample purity, as in the case of gadolinium. We have, however, plotted C_p vs. β curves using the data on the samples of highest purity. C_p values were taken from smoothed curves of Krauss and Warncke[22] and β values from the curves of Williams[54] for sample I (as designated in his paper). The C_p versus β plot is given in figure III. The values of DT/DP calculated from the asymptote is 0·35°C/kbar, which agrees well with the experimental value of 0·35°C/kbar as reported by Patrick[32]. The exact numerical agreement should not be taken too seriously as there is an uncertainty of about 10% in estimating the asymptote in figure III.

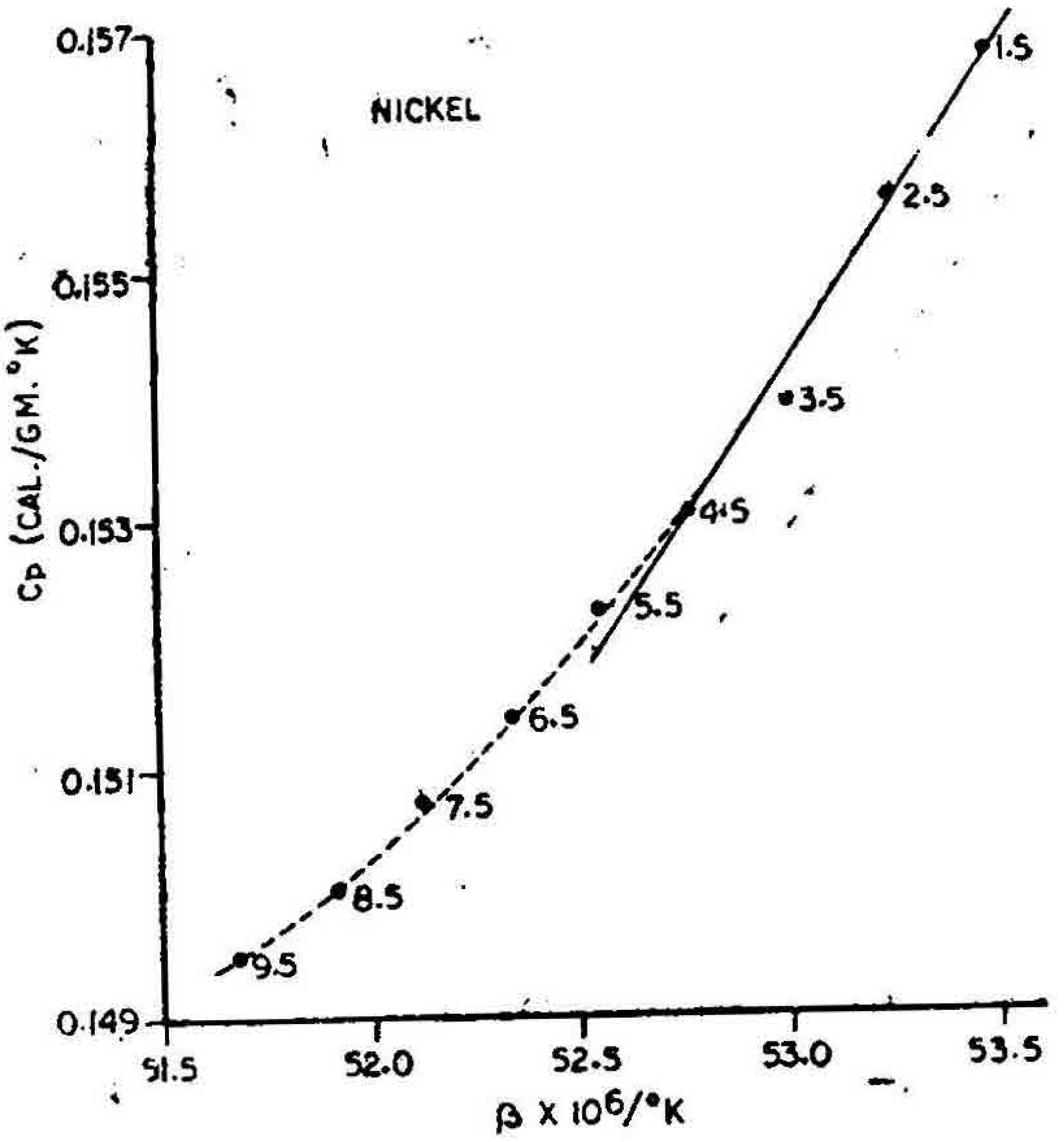

FIG. III

C_p versus β of nickel. The values of $|T_c - T|$ are indicated in °K near the points.

RESULTS FOR ANTI-FERROMAGNETIC TRANSITIONS

The values of specific heat near Neel temperature are available for a number of antiferromagnetic substances FeF_2, COF_2, NiF_2, MnF_2, MnO, FeO, MnTe, $MnCO_3$, Cr and others. The experimental measurement of DT/DP has been carried out for MnF_2, COF_2, MnTe, $MnCO_3$, $CoCO_3$, Cr and some other substances. Good thermal expansion values are however not available for many substances and it is the main limitation in testing the first Pippard relation (*eq.* 3). This relation has been tested for $T < T_N$, in the present study, for MnF_2, MnO and MnTe for which the necessary data are available. Using the measured values of compressibility and cubical thermal expansion of *Cr*, the second Pippard relation (*eq.* 4) has also been verified.

MANGANESE FLUORIDE

The anomalous specific heat of MnF_2 was first reported by Stout and Adams[44]. Accurate measurements of specific heat near T_N (– 67°K) were later carried out by Stout and Catalano[45], Hofman et al.[20] and Teaney[47]. The volume expansion coefficients of MnF_2 have been measured by Astrov et al.[1] and Sirota et al.[42] The plots of C_p vs. β were obtained by using

Teaney's data on C_p which extends to within a few millidegrees of T_N, and the β values taken from the smoothed curves of Astrov et al. The slope of this plot (figure IV) gives $DT/DP = 0{\cdot}32°$/kbar for MnF$_2$. This value is in a good agreement with experimental values $(0{\cdot}30 \pm 0{\cdot}02)$°C/kbar obtained from the dependence of F-19 n. m. r. resonance frequency in MnF$_2$[3] and $(0.303 \pm 0{\cdot}03)$°C/kbar, obtained from the n. m. r. measurements close to T_N[19] It appears that the estimate of Astrov et al[1] $(0{\cdot}8 \pm 0{\cdot}1)$°/kbar, from the measurement of susceptibility as a function of temperature at two different pressures, is rather high and their discussion based on Ehrenfest relations is open to objection.

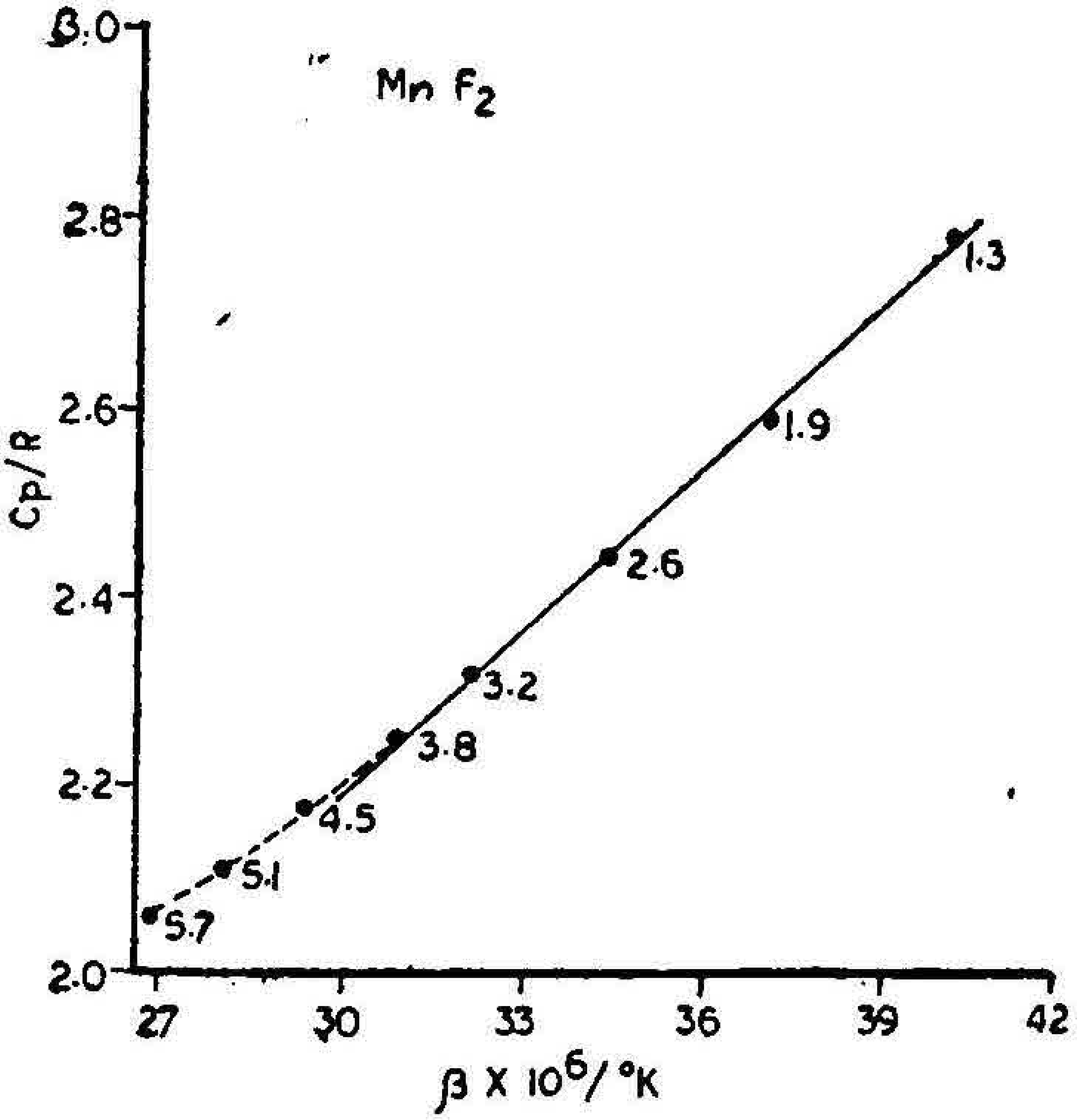

FIG. IV

C_p versus β plot for manganese fluoride.

MANGANESE OXIDE AND MANGANESE TELLURIDE

To obtain C_p vs. β plots, the values of specific heat near T_N were taken from the work of Kelley[21] on MnTe and Millar[28] on MnO. The volume expansion coefficients were taken from the smoothed curves of Grazhdankina and Gurfel[17] for MnTe and those of Foex[11] on MnO. DT/DP for MnTe calculated from these plots is $4{\cdot}0$°C/kbar which is of the same order as the experimental values 2.0°C/kbar[12] and $2{\cdot}6$°C/kbar. The experimental observations of C_p and β do not extend close to T_N and are available upto $T_N - T \sim 2$°C in the case of of C_p and $T_N - T \sim 4$°C in the case of β. So it is possible that

C_p vs β plot has not reached its asymptotic DP/DT value. Further $T_N = 307°K$ as reported by Kelley and $T_N = 310°K$ as reported by the Russian workers are significantly different.

To our knowledge, the value of DT/DP from the experimental measurements is not available for MnO. On the basis of equation (3) a value $DT/DP = 1{\cdot}4°C/kbar$ is predicted.

CHROMIUM

The values of adiabatic compressibility of chromium in the vicinity of T_N were determined by Bolef and de Klerk[6] from measurements of the velocity of ultrasonic wave propagation. The adiabatic compressibility can also be estimated from the values of Young's modulus and Poisson's ratio measured by Robertson and Lipsitt[38] on polycrystalline samples of high purity chromium· Using the compressibility values from the more recent work of Robertson and Lipsitt[38] and β from the work of White[53].: the plot of k vs β was obtained (fig. V). Close to Neel temperature ($= 311°K$) the plot is linear, in consonance with the Pippard second relation (*eq.* 4).

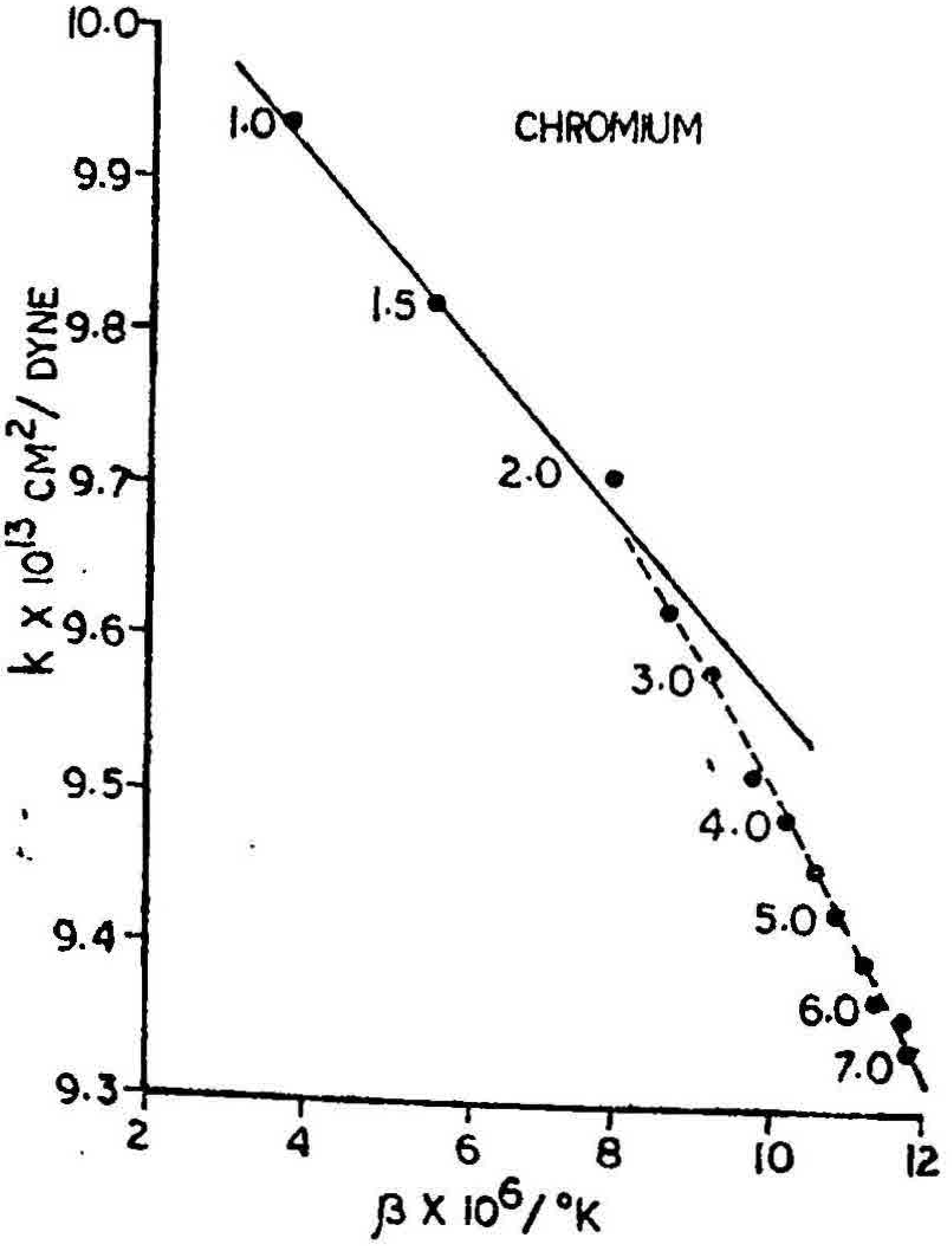

Fig. V

Compressibility of chromium as a function of the coefficient of volume expansion.

The value of DT/DP calculated from the plot is $-5.8\ ^\circ C/kbar$. The measured value of DT/DP from neutron diffraction at high pressures is $-6.0\ ^\circ C/kbar$[24], from the acoustic velocities is $-5.6\ ^\circ C/kbar$[49] and from electrical resistivities is $-(5.1 \pm 0.2)\ ^\circ C/kbar$[29]. These values are in good agreement with the value obtained from Pippard relations.

DISCUSSION

At present the thermal expansion values near the transition temperature are available only for a few substances. Therefore it is not possible to carry out exhaustive correlations among the thermodynamic data. It is, however, abundantly clear from the examples given here that the Pippard relations are borne out near magnetic phase transitions. The values of DT/DP, calculated from the plots of thermodynamic quantities appearing in the Pippard relations, agree well with the directly measured values.

The present method of correlating the thermodynamic properties and the pressure variation of transition temperature is free from the shortcomings of Ehrenfest approach. The Pippard relations are obtained from the cylindrical approximation of the entropy surface in the vicinity of transition temperature for λ-type transitions[35]. These relations can also be derived if analyticity of entropy surface near the transition temperature is assumed[7]. Thus irrespective of the nature of phase transitions the Pippard relations can be applied in general, but the same cannot be said of Ehrenfest relations.

Further the Pippard relations refer to a single phase and this is an advantage in discussing the experimental measurements. It is known, for instance, that on the high temperature side the approach to infinity is over a rather small interval of temperature and consequently the accuracy of the experimental observations is low. This is in fact the reason why the Pippard relations are easily tested for $T < T_\lambda$ in most cases. It is only in a few cases, such as helium, that data of sufficient precision exist for $T > T_\lambda$. The absence of data above T_λ, in ordinary materials, gives considerable uncertainity in locating the asymptote of the C_p *vs.* β and other plots. Such a difficulty does not arise in the He^4 case and the asymptote is clearly defined.

In the case of gadolinium the plot of C_p *vs.* β for samples of different purity support the conclusion that the purity of sample is of vital importance in determining the thermal properties of magnetic materials near T_c. Similar sample-to-sample variations exist for Ni and Cr. Indeed even the transition temperatures may be different as was the case with MnTe. Therefore it would be very desirable to perform all the measurements of C_p, β, k_T and DT/DP on the same sample and for the substance, on the samples of different purity. It would make a critical examination of Pippard relations possible and would also exemplify the effects of sample purity on the thermal properties of the magnetic materials. At present such data are lacking. So in comparing the values of DP/DT calculated from the Pippard relations and those obtained from the direct measurements, it should be remembered that if these values refer to different samples, they will be some what different. The correlations reported in the present work refer to the samples of highest (quoted) purity.

Finally it should be pointed out that at present the data on specific heat near T_c are generally more accurate than the data on β and k_T. Considerable progress would be made if the thermal expansion and elastic constants could be determined sufficiently close to the transition temperatures. A programme of work along these lines is being initiated here with the financial support of C.S.I.R. and the present work espouses the dire need for such studies.

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