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Exciting Developments in the Thermophysics of the Pnictides and Chalcogenides of the Transition Elements

E.F.Westrum Jr.

A terse reexamination of the thermophysical aspects of the chemical thermodynamics of the transition element chalcogenides is presented with a view to updating the Grønvold and Westrum approach of 1962. A somewhat more detailed progress report and insight into the situation pertaining to the transition element pnictides is also pursued in order to attain an impression of the similarities and differences between these two important classes of transition element compounds.
The increasing availability of high-temperature adiabatic calorimetric data to supplement that obtained by cryogenic calorimetry, a better appreciation of the dilatometric contribution (especially important as higher temperatures are considered), the effect of band structure and related problems are reviewed, and interesting examples of these and other phenomena are presented for a few selected substances including marcasite, cobalt ditelluride, iron diantimonide, chromium diantimonide, chromium monoarsenide, triuranium tetraarsenide and tetraantimonide, uranium diantimonide, diarsenide, and low-digenite ($Cu_{1.80}S$).
The bibliography includes 90 references.

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At the very outset I would like to express my appeciation to the Organizing Committee of the All-Union Conference on Calorimetry (Moscow, 1977) and to the Academy of Sciences of the U.S.S.R. for providing this opportunity for us to meet together and to discuss progress on thermodynamic projects of mutual concern. I can remember well my first participation in the third of these impressive meetings and in the intervening conferences as well and hope that there will be many more as it is clearly to the mutual advantage of the advancement of our projects to learn of new developments—but more important—it results in an accelerated achievement of progress towards our ultimate goals. The excellence of the papers presented and the enthusiasm of the participants attests to the careful planning by the Organizing Committee.

I. PERSPECTIVE AND INTRODUCTION

Approximately a decade and a half ago, Grønvold and Westrum, in the first issue of the then new Journal, "Inorganic Chemistry", presented an extensive paper concerned with the correlation and estimation of the entropies of the transition element chalcogenides[1]. By way of reminder, the most striking outcome of this analysis involved the fact that the cationic entropy contribution according to Latimer[2], instead of increasing gradually and continuously in a monotonic logarithmic aspect, leveled off essentially in "shelves" for each of the successive n-levels of the principal "d" quantum numbers as shown in Fig. 1. Although this approach was not adopted by Mills in his mammoth compilation of the thermodynamics of the sulphides, selenides, and tellurides[3], we are undaunted as to its essential correctness and believe that he did not detect it primarily because he was using equilibrium as well as the direct adiabatic calorimetric determination of entropies and simply did not, therefore, enjoy the same high precision of resolution that was possible to us. As a matter of fact, a recent application of this scheme to the lanthanide halides has done much to verify its essential correctness insofar as the lanthanides are concerned[4,5].

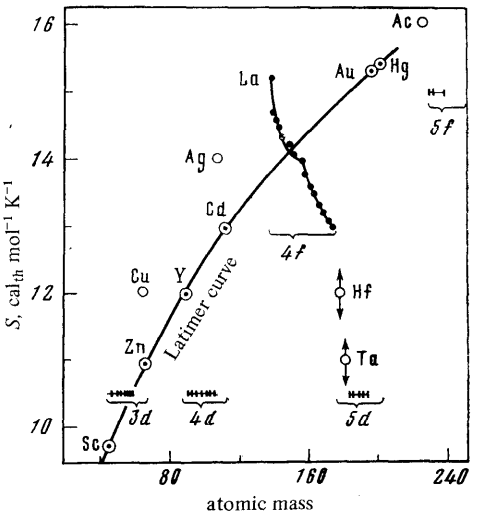


Figure 1. Modification of the Latimer cation scheme for transition[1], lanthanide[6], and actinide[1] elements.

In surveying the progress that has been made in this area subsequent to 1962, we note particularly that more than anything else the era is characterized by a relatively slow accumulation of data on the transition-element chalcogenides. Only within the last two years have F. Grønvold and the author been involved once again in this study and most of this work remains as yet unpublished. Some idea of the recent progress is summarized in Table 1; the most important new development has been the determination of the higher-temperature heat capacities by adiabatic calorimetry done primarily by Grønvold at Oslo.

Table 1. Chalcogenides and pnictides for which Third-Law entropy data have recently been obtained in the author's laboratory.

Chalcogenides			Pnictides		
	3*d*			3*d*	
FeS_2 (marcasite)	$CoTe_2$ NiS	$Cu_{1.00}S$ (covellite)	CrAs	FeAs	NiAs
	$CoSe_2$	$Cu_{1.75}S$ (anilite)	CrSb		
		$Cu_{1.80}S$ (low-digenite)	$CrSb_2$		
		$Cu_{1.96}S$ (djurleite)		5*f*	
		$Cu_{2.00}S$ (chalcocite)	$ThAs_2$		UAs_2
	4*d*		$ThSb_2$		USb_2
$RuSe_2$		Ag_2S			U_3As_4
	5*f*				U_3Sb_4
$ThSe_2$					

In considering a similar (preliminary) survey of the transition element pnictides we find that the availability of high-temperature data is an important aspect. In some ways many of these compounds are more metallic than the corresponding chalcogenides, and band structures replace the convenient discrete electronic levels characteristic of many of the chalcogenides. This involved new problems of interpretation and correlation. At the present time, thermophysical data on a baker's dozen of these have been generated—primarily through our own endeavours—and we continue to pursue enthusiastically these very interesting substances. It is too soon yet to attempt a true overview, but this paper will present some of the interesting developments which have thus far been encountered in both classes of compounds. In the presentation which follows an arbitrary selection of the results has been made to emphasize particularly the interesting phenomena encountered over high- and low-temperature ranges in both chalcogenides and pnictides. Hopefully, the time will soon be ripe for a more detailed analysis and correlation of the pnictides. I want to emphasize that without the great skill in synthesis that has been developed at the Kjemisk Institute at Oslo, initially under Professor Haakon Haraldsen and more recently by Dosent Grønvold, neither temperature range could have been covered with assurance that the materials were "well characterized". The work has been materially accelerated by other collaborators as noted in the acknowledgement.

II. CONTRIBUTIONS TO THE HEAT CAPACITIES

A perpetual endeavour in our studies is first of all to understand the resolution of the heat capacity into the several most important contributions involved. This resolution, based in part upon knowledge of the compound from other auxiliary techniques, is important, not merely as an exercise in itself, but also as a means of enhancing our ability to estimate the thermodynamic properties of transition elements, chalcogenides, and pnictides. We may consider the observed heat capacity to be a sum of the following contributions:

$$C_p = C_v(l) + C(e) + C(m) + C(s) + C(d).$$

Here $C_V(l)$ is the lattice-vibrational heat capacity at constant volume, $C(e)$ the conduction electron contribution, $C(m)$ the cooperative magnetic contribution from population of excited electronic states, $C(s)$ the Schottky contribution, and $C(d)$ the dilation contribution. In transition regions the various contributions may be coupled, but the feasibility of their separation is assumed.

Lattice heat capacity at constant volume. This prime contribution to the heat capacity may usually—in the absence of more detailed information—be expressed by a single Debye function with constant characteristic temperature, Θ_D, for a simple monatomic substance, or by a sum of Debye and Einstein functions for a compound. As a first approximation, the higher-temperature heat capacity is often calculated after evaluating an effective Debye temperature from the heat capacity over the 50 to 100 K region.

Conduction electron contribution. The molar electronic contribution to heat capacity is in the first approximation proportional to the thermodynamic temperature T and equal to

$$C_v(e) = \frac{4\pi^2 k^2 m T N_A}{h^2 (3\pi^2 N/V)^{2/3}} = \gamma T,$$

where k is the Boltzmann constant, m the electron rest mass, L the Avogadro number, h the Planck constant, and N/V the number of electrical carriers per unit volume. The γ's calculated from electrical measurements are, however, often smaller than those derived from low-temperature, heat-capacity measurements.

Magnetic and Schottky contributions [$C(m)$ and $C(s)$]. These contributions often occur either as a cooperative transition from a magnetically ordered state (ferro-, ferri, antiferro-, or heli-magnetic state) or from a gradually changing electron distribution with temperature, i.e. a Schottky transition. For the former case, the magnetic entropy change is related to the changes in the observed magnetic moment or to susceptibility below and above the transition, but the interpretation is still uncertain in most cases. The molar heat capacity from a non-cooperative, Schottky-type transition can be expressed as

$$C(s) = RT\partial^2\{T \ln \Sigma g_i \exp(-E_i/kT)\}/\partial T^2,$$

where g_i is the degeneracy of the ith level, separated from the ground level by an electronic energy E_i. Differentiation yields an expression suitable for computer calculations[6]:

$$C(s) = (1/RT^2)\left[\frac{\Sigma E_i^2 g_i \exp(-E_i/kT)}{\Sigma g_i \exp(-E_i/kT)} - \left\{\frac{\Sigma E_i g_i \exp(-E_i/kT)}{\Sigma g_i \exp(-E_i/kT)}\right\}^2\right].$$

This contribution should by no means be regarded as important only at very low temperatures. Sommers and Westrum have shown it to be important above 300 K also[4,5]. Furthermore, the paper by Rakhmenkulov et al.[7] presented at this meeting has provided much interesting information on lanthanide phosphides.

The dilation contribution. In general, this contribution is

$$C(d) = C_p - C_v = \alpha^2 VT/\beta,$$

where α is the thermal expansivity, V the molar volume, T the thermodynamic temperature, and β the isothermal compressibility. When the thermal expansivity is known, but not the compressibility, the dilation contribution can be estimated by use of the Grüneisen relation:

$$C(d) = \alpha\Gamma C_v T,$$

where the Grüneisen parameter Γ is chosen on the basis of values for related substances. A better estimate is obtained when both α and β have been determined at one and the same temperature but Γ is in general slightly temperature dependent. When neither α nor β is known—the dilation contribution may be estimated according to Nernst and Lindemann as

$$C(d) = AC_p^2 T/T_f,$$

where the "universal" constant $A = 0.005$ J^{-1} K for one gram-atom and T_f is the melting temperature of the substance.

III. CALORIMETRIC TECHNIQUE

Heat capacity measurements were made in a Mark II adiabatic cryostat over the 50 to 300 K region at the University of Michigan. This cryostat was described previously[8]. The samples were contained in gold-plated copper calorimeters which incorporated a gold-gasketed seal and gold-plated copper vanes to enhance conductivity. Temperatures were measured with a platinum, capsule-type, 25-ohm (nominal) resistance thermometer inserted into a re-entrant well in the calorimeter.

The calorimetric apparatus and measuring technique for the region 300 to 1030 K at the University of Oslo have been described[9]. The calorimeter was intermittently heated, and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed silica glass tube of about 50 cm^3 volume, tightly fitted into the silver calorimeter. A central well in the tube served for the heater and platinum, resistance thermometer.

The cryogenic thermometer had been calibrated by the U. S. National Bureau of Standards, and that for the high-temperature calorimeter locally, at the ice, steam, tin, zinc, and antimony points. Temperatures are judged to correspond to IPTS-68 within 0.03 K from 5 to 300 K and within 0.05 K between this temperature and 900 K. The uncertainty rises to 0.2 K at 1030 K. Resistance, energy, and mass were measured with reference to calibrated instruments by the U. S. National Bureau of Standards.

The heat capacities of both types of empty calorimeters were determined in separate series of experiments. It is emphasized that both sets of measurements were made by adiabatic calorimetry and that equilibrium was typically achieved in all determinations.

IV. MARCASITE/PYRITE METASTABLE TRANSFORMATION

One of our most satisfying publications of 1976 has been the resolution of the stability of marcasite vis-ã-vis pyrite[10]. As is well known, iron disulphide occurs in nature (and can be prepared in the laboratory also) in two polymorphic forms, marcasite and pyrite. While a considerable amount of thermodynamic data exists for pyrite[3,11], such data are virtually unknown for marcasite, except for some measurements of its enthalpy of combustion[12-14]. In order to remedy this situation and to evaluate the stability conditions for the polymorphs, the heat capacity of marcasite has been determined from 5 K to the temperature region where it transforms into pyrite. Measurements on the previously studied pyrite sample[1] have been extended to 770 K.

The heat capacity of the pyrite sample increased gradually over the temperature range 5 to 770 K without any sign of transformation[10]. The values were usually 0.1 to 1.0 per cent lower than for marcasite at the corresponding temperature. The higher-temperature, heat-capacity measurements on marcasite were quite normal until an energy input produced a somewhat higher temperature increment and brought the temperature up to 706.43 K. Here the drift-rate gradually changed from a slightly negative value of about -0.0009 K min^{-1} to large positive values after a period of 2 h. The subsequent gradual temperature increase was followed for a further 96 h, at which time the temperature was estimated to be not more than (0.15 ± 0.25) K from the limiting value T_∞.[15] The enthalpy of transformation of marcasite to pyrite at 700 K is $\Delta H^\circ_{tr} = (-1050 \pm 50)$ cal$_{th}$ mol^{-1}†. When the heat-capacity measurements were continued after 96 h, the heat capacity corresponded closely to that of pyrite, and X-ray powder photographs taken of the sample after completion of the measurements showed the presence only of pyrite.

In the absence of a zero-point entropy in this system, marcasite even in the vicinity of the transformation temperature is thermodynamically metastable with respect to pyrite. Since the transformation is monotropic and irreversible, we cannot ascribe an entropy increment to the transformation and instead utilize an enthalpy cycle for the marcasite-pyrite system through $T = 0$. Taking into account the enthalpy increment for the marcasite to pyrite transformation to 700 K, $H(T = 0,$ marcasite$) - H(T = 0,$ pyrite) is found to be (0.99 ± 0.05) kcal$_{th}$ mol^{-1}. This value should, therefore, be incorporated into $[G^\circ(T) - H^\circ(0)]/T$ for marcasite for chemical thermodynamic calculations. Moreover, marcasite is seen to be clearly metastable with respect to pyrite above $T = 0$. For example, at 298.15 K the value of ΔG° (marcasite → pyrite) is (-0.95 ± 0.05) kcal$_{th}$ mol^{-1}.

Our results together with the critically evaluated values of ΔH_f°(pyrite) from Mills'[3] and from Robie and Waldbaum's[12] reviews together with entropies for iron[16] and sulphur[17] yield the following standard enthalpies, entropies, and Gibbs energies of formation of FeS_2 at 298.15 K:

		Pyrite	Marcasite
$\Delta_f H^\circ$,	kcal$_{th}$ mol^{-1}	-41.5 ± 0.5	-40.5 ± 0.5
$\Delta_f S^\circ$,	cal$_{th}$ K^{-1} mol^{-1}	-9.07 ± 0.10	-8.84 ± 0.10
$\Delta_f G^\circ$,	kcal$_{th}$ mol^{-1}	-38.8 ± 0.5	-37.9 ± 0.5

The geological occurrence of pyrite pseudomorphs after marcasite is consistent with above interpretation, since

† Throughout this paper, cal$_{th}$ = 4.184 J.

marcasite presumably occurs in low-temperature hydrothermal deposits and apparently occasionally transforms into pyrite at temperatures well below 700 K.

V. COBALT DITELLURIDE AND COBALT DISELENIDE

We have determined the heat capacity of another compound of marcasite-type structure—orthorhombic cobalt ditelluride—from 5 to 1030 K by adiabatic-shield calorimetry with intermittent energy inputs and equilibration. It shows interesting behaviour [18].

Its paramagnetism indicates the presence of unpaired 3*d*-electrons. The effective magnetic moment (2.2 μ_B at 720 K) [19] is much smaller than the moment (3.87 μ_B) expected for Co^{2+} in the high-spin state and somewhat higher than the value 1.73 μ_B for the low-spin state in the configuration spin-only approximation. The intermediate moment observed is possibly due to orbital contributions of the kind commonly observed in the case of Co(II) complexes. Hence, the effect of orbital ordering might be observable in the heat capacity of $CoTe_2(m)$ just as predicted [20] for the related ferromagnetic case and observed for $CoS_2(p)$‡.

According to Goodenough [21], $CoTe_2(m)$ contains one itinerant 3*d*-electron in a σ^*-band sufficiently wide to preclude cooperative magnetic ordering. Overlap of this band with a σ^*-band of the anions was suggested as an explanation of the non-stoichiometry of the $CoTe_{2+x}$-phase. The Vandenbempt alternative view [22] presupposes antiferromagnetic ordering in $CoTe_2(m)$, by analogy with the assumption made for $CoSe_2(p)$ by Adachi et al. [23] However, neither the present heat-capacity measurements, nor the Mössbauer experiments by Kjekshus and Nicholson [24] indicate the presence of cooperative ordering or magnetic exchange interactions due to localization of 3*d*-electrons into sub-bands.

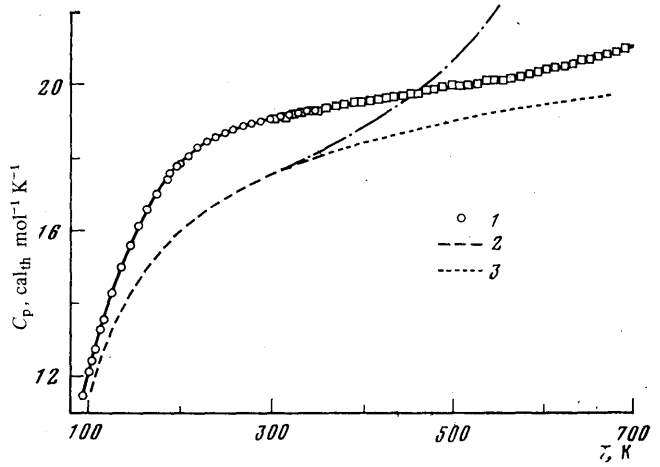


Figure 2. Molar heat capacity of $FeSb_2$ from 100 to 700 K compared with that of $FeTe_2$. ○, Results for $FeSb_2$ from low-temperature calorimetry; □, results for $FeSb_2$ from high-temperature calorimetry; ---, results for $FeTe_2$ by Westrum et al. [25], –·–·–, results for $FeTe_2$ by Mikler et al. [26], ----, extrapolated lattice heat capacity of $FeTe_2$.

‡ *m* = magnetic; *p* = paramagnetic.

No lattice-dynamical analysis has yet been carried out. In analysing the thermophysical properties of $CoTe_2$, we therefore used the experimental heat capacity of $FeTe_2$ [25]—a rate isostructural analogue of $CoTe_2$. This compound is non-magnetic, has semiconducting properties and its atomic masses, interatomic distances, and angles are almost identical with those of $CoTe_2$. Thus, the excess heat capacity of $CoTe_2(m)$ relative to $FeTe_2$ might be related to differences in the outer electronic structure rather than to differences in the lattice contributions. The excess heat capacity rises to a rather pronounced maximum of 1.7 cal_{th} mol^{-1} K^{-1} at 80 K and then falls gradually with increasing temperature. It may reflect a large increase in density of states just above the Fermi level, and thus the presence of levels or bands with high-density regions which presumably derive from the broader bands assumed by Goodenough [21] and by Vandenbempt et al. [22] In the absence of further details about the level and band structure of $CoTe_2(m)$, it remains to be investigated whether the lowest excited level or band is primarily an antibonding σ^*-metal state, an overlapping-anion, *p*-band state, or of other origin.

The resemblance of the excess heat capacity to a Schottky-type transition is illustrated in Fig. 2 on the assumption of two excited levels 65 and 175 cm^{-1} above the ground level with degeneracies $g_0 : g_1 : g_2 = 1 : 1 : 3$. The rather good fit in the region up to 100 K cannot be taken as a proof of the uniqueness of the explanation, but even so, the model might approximate the variation in the density of states. Because of uncertainty in the assumptions, the introduction of further levels to account for the deviation above 100 K has not been attempted.

Since it is well known that Schottky-like heat capacity contributions occur also as differences between Debye and/or Einstein functions with different characteristic temperature, the metallic nature of $CoTe_2(m)$ might give rise to a lower characteristic temperature than that for $FeTe_2$ and a more rapid heat capacity rise will then be expected at intermediate temperatures. This alternative interpretation of the excess heat capacity is also illustrated in Fig. 2, assuming (constant) Debye temperature of 300 K for $FeTe_2$ and 250 K for $CoTe_2(m)$.

Interestingly, the estimated value for the entropy calculated through the cationic and anionic entropy contributions [1] for solid transition-metal chalcogenides is 24.0 cal_{th} mol^{-1} K^{-1} at 298.15 K, or about 3.4 cal_{th} mol^{-1} K^{-1} lower than that observed. This result is analogous to those for other cobalt and nickel chalcogenides as a consequence of the neglect of the contributions from population of low-lying electronic states or bands, which we thus far had been unable to evaluate properly.

The heat capacity increase for $CoTe_2$ above 300 K follows a different pattern from that observed for $FeTe_2$. [26,27] An unusual increase is observed of a temperature as low as 400 K in the latter, probably occasioned by defect formation as in $FeSe_2$, [28] while for $CoTe_2(m)$ only a gradual increase in heat capacity, primarily due to the dilational term is observed up to 900 K. Above this temperature a sigmoid increase is noted from about 23 cal_{th} mol^{-1} K^{-1} at 930 K to about 33 cal_{th} mol^{-1} K^{-1} at 1030 K. This reflects the precipitation of the $Co_{1-x}Te$-phase from stoichiometric $CoTe_2$ as the peritectic decomposition temperature for the $CoTe_2(m)$-phase is approached.

The entropy of $CoTe_2(m)$, the entropies of the elements [29], and the enthalpy of formation of $CoTe_2(m)$ (found by solution calorimetry) [30], have been determined and their

values for $CoTe_2(m)$ at 298.15 K are:

$\Delta_f H^0$, $kcal_{th}\ mol^{-1}$	-17.44 ± 0.7
$\Delta_f S^0$, $cal_{th}\ mol^{-1}\ K^{-1}$	-4.37 ± 0.3
$\Delta_f G^0$, $kcal_{th}\ mol^{-1}$	-16.1 ± 0.8

The latter two values are at variance with those determined by Komarek et al.[30] from decomposition pressures.

Measurements on $CoSe_2$ have thus far revealed only a simple approximately sigmoid heat capacity over both low- and high-temperature regions[31].

VI. THERMOPHYSICAL PROPERTIES OF $FeSb_2$

Let us consider $FeSb_2$ as one example—not necessarily totally typical—of the problems encountered in this endeavour. Electrical and magnetic measurements on well-characterized samples of $FeSb_2$ by Fan et al.[32] led them to conclude that $FeSb_2$ is a semiconductor or a semimetal with an extremely narrow band gap. Further support was provided by the study of the Mössbauer effect from 6.4 to 560 K by Steger and Kostiner[33] who fitted their data to a function indicating that the temperature dependence of the quadrupole splitting is the result of an electrical process which involves the thermal population of an empty conduction band. Hence, the study of the heat capacity of $FeSb_2$ would offer conclusive evidence for the absence of cooperative phenomena in the compound, and also show the effect of band population.

The heat capacity of $FeSb_2$ increases quite monotonically over the entire temperature region and with little evidence of preperitectic decomposition[34]. This contrasts with the X-ray diffraction results by Fan et al.[32] that $FeSb_2$ decomposes into FeSb and Sb under vacuum at 573 K. The decomposition found here (1021.2 ± 0.2) K is in complete agreement with that found by Geiderikh et al.[35] (1021 K) while the results of Kurnakov and Konstantinov[36] (1001 ± 2 K) and Holseth[37] (1004.6 ± 0.5) K are considerably in error.

No trace of the antiferromagnetic transition claimed to exist around 800 K to 1000 K by Rosenqvist[38] and by Holseth and Kjekshus[39] was detected, which accords with the observation by the latter authors that no purely magnetic reflections were obtained in their neutron-diffraction study of $FeSb_2$ around 300 K. Thus, iron is accordingly in a non-magnetic ground state, which presumably arises from the $3d^4$ configuration. The ΔH_d for the peritectic decomposition at 1021.2 K is $(12\,910 \pm 30)\ cal_{th}\ mol^{-1}$.

However, the heat capacity of $FeSb_2$ does not show the pronounced increase at higher temperatures characteristic of $FeTe_2$[26,27] (see Fig. 2). Similar behaviour in $FeSe_2$ has been attributed to defect formation[28], while neither isostructural FeS_2[10] nor isoelectronic $NiSb_2$[40] show comparable excess heat capacities in the higher-temperature region. A comparison of $FeSb_2$ and $FeTe_2$[41] has already been made.

In the Goodenough[42] and the Fan et al.[32] model the $3d$-electron b-band is filled with four electrons, while the next doubly degenerate $a_\parallel$-band is empty. Steger and Kostiner[33] concluded from the unusual temperature dependence of the Mössbauer quadrupole splitting that electrons were promoted across an energy gap of only (33 ± 1) meV (or 265 cm^{-1}), that is, having approximately the same value as that derived by Fan et al.[32] from electrical conductivity measurements ($\sim 210\ cm^{-1}$). If the band is assumed to be narrow and its population approximated by a Boltzmann distribution, we find that excitation from a fourfold-degenerate b-band does not produce the observed increase in heat capacity. Thus, either the b-band might be split, or further levels or bands in addition to $a_\parallel$ and σ^* are also being populated. We are not at this time able to make a decision between the various alternatives, but should like to remark that a surprisingly good agreement is obtained (see Fig. 3) if a split $(2)b$-band is succeeded by $(2)a_\parallel$ and $(4)\sigma^*$ (in Goodenough's model) with $E_1/hc = 200\ cm^{-1}$ and $E_2/hc = 500\ cm^{-1}$.

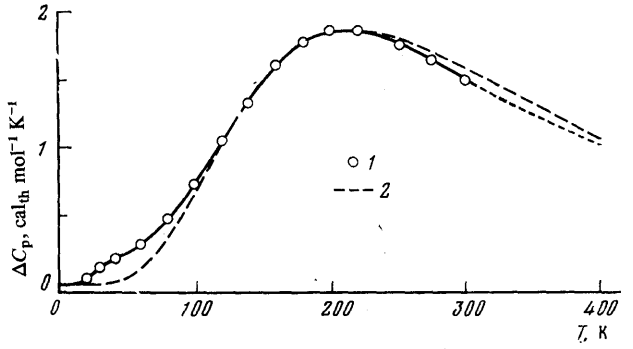


Figure 3. o, Excess molar heat capacity of $FeSb_2$ relative to that of $FeTe_2$. – – –, Calculated Schottky heat capacity for $E_1/hc = 300\ cm^{-1}$, $E_2/hc = 500\ cm^{-1}$, and $g_0, g_1, g_2 = 1, 1, 2$.

VII. CHROMIUM DIANTIMONIDE

The magnetic properties of chromium diantimonide with orthorhombic marcasite-type structure[43] show a maximum in susceptibility of $CrSb_2$ around 600 K and indicate the presence of two unpaired spins per chromium atom at high temperatures, and hence of formally quadrivalent chromium in $CrSb_2$. It was mentioned already by Foex and Graff[44] that $CrSb_2$ showed antiferromagnetic behaviour just as does CrSb, but no evidence was presented. In a later susceptibility study by Holseth and Kjekshus[39] the unusual susceptibility behaviour was confirmed and it was suggested that $CrSb_2$ might be antiferromagnetic with a Néel temperature close to the decomposition temperature. But Adachi et al.[45] interpreted their susceptibility measurements over the range 77 to 900 K in terms of the excitation of electrons from a singlet-to a triplet-spin state with an energy separation of 0.07 eV. The same value of the energy gap was derived from low-temperature resistivity measurements. Accordingly, a broad, Schottky-type heat-capacity maximum of 2.03 $cal_{th}\ mol^{-1}\ K^{-1}$ at 288 K was expected. Adachi et al.[45] carried out heat capacity measurements only above 330 K and the results failed to confirm the correctness of their model.

In view of possible antiferromagnetic spin ordering, Adachi et al.[45] carried out neutron diffraction experiments near 300 K, but did not observe any magnetic reflections. Similar experiments by Holseth et al.[46] showed antiferromagnetic ordering at 4.2 K with doubled cell dimensions in the b- and c-directions. The magnetic spin quantum number is 0.97 per chromium atom and the magnetic moments are coupled parallel in each 011 plane of the magnetic unit cell, but in opposite directions in adjacent planes and with

orientation approximately normal to the 101 plane. Interestingly—of all the compounds with marcasite-type structure—$CrSb_2$ is the only one which shows clear evidence of magnetic ordering. In view of the observed cooperative ordering, a study of the heat capacity behaviour of $CrSb_2$ in the critical region seemed especially interesting. In addition, the increase in magnetic susceptibility to a maximum value around 600 K should also be reflected in the heat capacity and not result in a linear temperature relationship of the kind reported by Adachi et al.[45]

From the randomization of the spins of the two unpaired electrons revealed by magnetic susceptibility and neutron diffraction (neglecting further contributions from orbital states), a magnetic entropy $S_m = R \ln 3 = 2.17$ cal_{th} mol^{-1} K^{-1} is obtained, since the heat capacity of $CrSb_2$ (shown in Fig. 4) shows a small, sharp λ-type transition with a maximum at 274.1 K, where the change from the antiferromagnetic to the paramagnetic state occurs on heating[47].

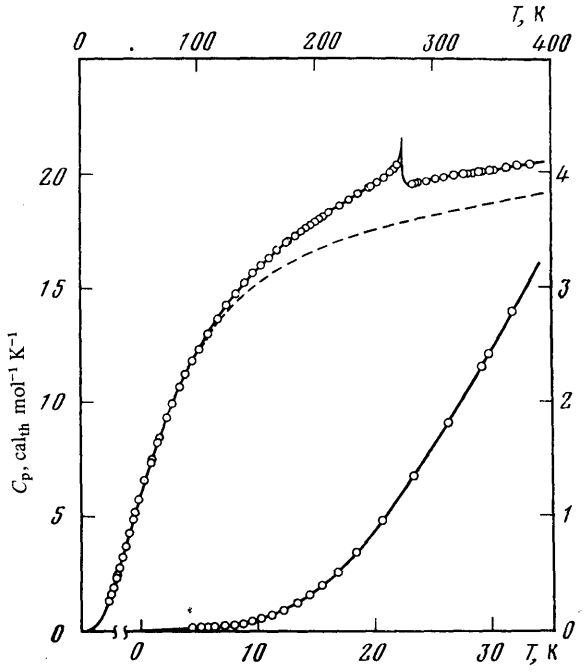


Figure 4. Heat capacity and antiferroelectric anomaly in $CrSb_2$; – – –, the estimated lattice contribution[47].

Obviously, only a fraction of this entropy (0.12 cal_{th} mol^{-1} K^{-1}) is generated in the clearly cooperative part of the transition. The heat capacity of $CrSb_2$ is, however, seen to be unusually high over a wide range in temperature above the transition at 274.1 K. This is evident by comparing it with those of the isostructural analogues $FeTe_2$,[41] $CoTe_2$,[48] and $FeSb_2$;[34] none of these are especially suited as "lattice heat-capacity models"—as they apparently differ substantially in vibrational properties, and the last two are also influenced by conduction-electron contributions. We, therefore, derive the lattice heat capacity of $CrSb_2$ from an estimate of its effective Debye temperature and by the application of a dilational heat-capacity term according to Nernst and Lindemann[49].

The constant Debye temperature used for calculating C_V(lattice) in the higher-temperature region was taken as the maximum of Θ_D in the lower-temperature region, $\Theta_D = 298$ K being obtained at 90 K. The dilational heat capacity is

$$C(d) = C_p - C_v = AC_p^2(T/T_m)$$

where the constant $A = 0.00713$ K mol cal_{th}^{-1} according to Nernst and Lindemann and $T_m = 991.3$ K is the peritectic decomposition temperature found here. Accordingly, the excess magnetic heat capacities are 1.7, 1.6, and 1.1 cal_{th} K^{-1} mol^{-1} at 300, 500, and 700 K respectively. Although this excess heat capacity was not observed by Adachi et al.[45], they nevertheless associated the magnetic behaviour with a transition from a singlet spin ground state to a split triplet state. Accordingly, a Schottky heat-capacity contribution with a maximum 2.03 cal_{th} K^{-1} mol^{-1} at 288 K should be observed.

Even though this model appears to fit the magnetic susceptibility data (disregarding the rather arbitrary subtraction of a temperature independent susceptibility term), it is not in agreement with the neutron-diffraction results, which point to the existence of two unpaired electrons per chromium atom in the ground state. According to our estimate, the total magnetic entropy up to 900 K is about 2.6 cal_{th} mol^{-1} K^{-1} or, well above this temperature, $R \ln 3 = 2.17$ cal_{th} mol^{-1} K^{-1}. In the search for further magnetic contributions the orbital components ought to be considered; according to ligand field theory the ground term of the d^2-configuration in an octahedral field is $^3T_{1g}$ with a total degeneracy $3 \times 3 = 9$. The exact splittings of the ground term are not known and in the zeroth approximation we assume that the first excited state (connected with the disappearance of cooperative magnetism) is a doublet, and that this state is followed by the remaining states, which might roughly correspond to a 3 : 6 Schottky heat-capacity contribution. Further consideration of this resolution is clearly a desideratum. Another point of interest concerns the composition of the $CrSb_2$ phase, but the original paper[47] will need to be consulted for that information.

VIII. CHROMIUM MONOARSENIDE

The heat capacity of chromium arsenide provides an interesting example of these AB compounds[48]. Here the heat capacity shows a distinct bell-shaped transition with a peak at 259.9 K related to the disappearance of antiferromagnetic helical ordering on heating. The entropy of this transition is 0.69 cal_{th} mol^{-1} K^{-1}. At 1170 K another transition is observed related to the phase change from the (300 K, stable) MnP-type to the NiAs-type structure. The entropy of the latter (gradual) transition is 0.077 cal_{th} mol^{-1} K^{-1}.

Chromium monoarsenide has been extensively studied by X-ray and neutron-diffraction, magnetic-susceptibility, and magnetization techniques, and two solid-state transitions have been described. The thermodynamic properties of CrAs are largely unknown, however, except for the heat capacity measurements by Kazama and Watanabe[50] in the region from 180 to 280 K. Our investigation was undertaken to improve and extend the earlier heat capacity data, thereby providing thermodynamic data for CrAs over the stability ranges of the solid phases, and, in particular,

to explore the detailed trends in the regions of both the low-temperature transformation and higher-temperature transition.

According to Haraldsen and Nygaard[51], the magnetic susceptibility of CrAs increases steadily over the region from 80 to 600 K, indicating an enhanced population of higher magnetic states. Yuzuri[52] found a peak in the susceptibility at 820 K which was taken to imply an antiferromagnetic to paramagnetic transition in this region, while Selte and Kjekshus[53] observed a further small increase in susceptibility in the region from 800 to 970 K. Above 300 K, one might then expect to encounter an excess heat capacity due to the population of excited electronic states in chromium and also a thermal effect accompanying the transformation of the MnP-type into the NiAs-type structure.

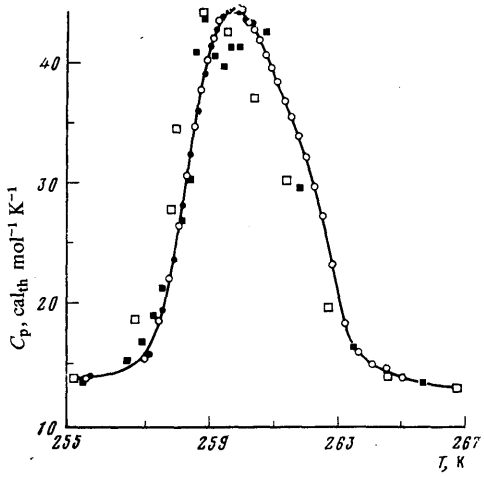


Figure 5. Heat capacity anomaly associated with double helical-spin ordering in $CrAs_2$.[48]

Below 300 K, a sudden structural change occurs in CrAs, which is related to a double helical-spin ordering with spiral propagation in the AB-plane. Watanabe et al.[54,55] reported that this occurred at about 280 K, while discontinuities in the lattice constants and anomalies in electrical resistivity and thermoelectric power occurred at 265 K. Selte et al.[56,57] observed the transition to go to completion at 272 K on heating, while the spiral structure reappeared at 261 K on cooling. According to Boller and Kallel[58], the transformation takes place in the range from 190 to 240 K and shows hysteresis and supercooling effects. The volume contraction on heating is accompanied by a shortening of the distance of one additional Cr-Cr contact considerably below the value r_c = 318 pm, which, according to Mott[59,60] and Goodenough[42], is the critical intermetallic distance for the localized-collective electron behaviour.

The heat capacity at the low-temperature transition is shown in Fig. 5. It rises to a rounded peak and then drops gradually with a shoulder on the high-temperature side. A cooling curve recorded at a rate of about 0.09 K min^{-1} shows that the sample does supercool by at least 6 K, as might be expected for a first-order transition.

In attempting to ascertain the thermodynamics of the magnetic ordering transition, we note that apparently none of the MnP-type pnictides is diamagnetic[61]. This makes it difficult to find an adequate lattice heat-capacity model among the isostructural analogues of CrAs, such as FeAs, CoAs, MnAs, and FeP. A further complication is that Schottky-type contributions to the heat capacity are anticipated above the transition. In order to estimate the lattice contribution, the heat capacity curve far below T_{tr} was connected smoothly to the C_p curve above the transition. The estimated lattice heat capacity is represented in Fig. 5 by a dashed line. With this lattice estimate, we find ΔS_{tr} = 0.69 cal_{th} mol^{-1} K^{-1} and ΔH_{tr} = 177 cal_{th} mol^{-1}. Watanabe et al.[54] report T_{tr} = 265 K and ΔH_{tr} = 124 cal_{th} mol^{-1} for this transition, determined by continuous heating adiabatic calorimeter. Despite the large differences in T_{tr} and ΔH_{tr} compared with our study, they report a shape of the transition curve that is quite similar to ours. The discrepancies in T_{tr} and ΔH_{tr} might be partly explained by the different methods used: dynamic versus equilibrium measurements—and differences in the lattice heat capacity, but probably differences in the nature nature of the samples are more important.

The value of the Néel temperature, T_{tr} = (259.86 ± 0.05) K, is not within the broad temperature range from 240 to 190 K assigned to the occurrence of the transition by Boller and Kallel[58] and is also much lower than the approximate value of 280 K reported by Watanabe et al.[54] from neutron diffraction studies.

Crystallographic and magnetization studies[58] have shown that the transition is of first order. The shape of the curve suggests that the order is higher but the hysteresis and long equilibrium times support the hypotheses of a first-order transition. Bean and Rodbell[62] presented a model for first-order magnetic transitions, in which the transition is shifted to higher temperatures as a consequence of the dependence of exchange interactions on interatomic distances and the volume change on transition.

IX. ACTINIDE PNICTIDES

U_3Pn_4 compositions. Attention has been drawn increasingly to the magnetic and thermophysical properties of uranium pnictides (U_3Pn_4) (in which Pn = P, As, Sb, or Bi), all of which have cubic Th_3P_4 structures. Magnetic susceptibility and magnetization measurements show that all of them are ordered to a ferromagnetic state below 300 K and that the Curie-Weiss law is obeyed above the Curie temperature (T_C) up to at least 400 K. The paramagnetic moment increases with increasing pnigogen size, but lack of such a correlation for the ordering temperature might indicate that the magnetic coupling is anomalously weak in U_3Pn_4.

For U_3X_4, the U^{4+} site has S_4-symmetry, which splits the ninefold degenerate $^3H_4$ ground term into five singlets and two doublets. Troc et al.[63] calculated the energy levels of the ground term using a point charge model and obtained a good correlation with their high-temperature magnetic susceptibility data. The lowest excited level, a singlet, is 9 cm^{-1} above the singlet ground level, and is followed by seven higher levels (the lowest of which is at 700 cm^{-1}).

So far we have only examined uranium arsenide and antimonide[64]; for the bismuthide and for the resolution of the problem of the low-temperature heat-capacity data for U_3P_4 reported by two authors—who disagree by a factor of two (!) as regards the entropy of transition—more work

is contemplated. Moreover, we need to study the heat capacities of the isostructural diamagnetic thorium analogues to be assured to a good resolution of the magnetic heat capacity.

Single crystals of U_3As_4 [64] are semimetallic with a resistivity of 290 pohm cm^{-1} at 300 K, while U_3Sb_4 is reported to be metallic [65]. Our electronic contributions are consistent with these interpretations.

It is well known that the magnetic contribution to the heat capacity cannot be easily separated from the total heat capacity [66]. Lacking heat-capacity data for diamagnetic Th_3As_4 and Th_3Sb_4, our estimate of ΔS_{tr} is somewhat arbitrary. Stalinski et al. [67] used the Heisenberg theory of spin-wave interactions [68] to estimate the magnetic heat capacity below $T_C/2$ for U_3P_4. We also used this method to establish the Debye-temperature curve at low temperatures, but, as pointed out by de Jongh and Miedema [69], this method can only be expected to be rigorous for insulating ferromagnets. Neutron-diffraction measurements [70,71] favour a non-collinear alignment of the spins and electrical resistivity measurements for U_3P_4 and U_3As_4 show a strong magnon conduction electron scattering [72].

From the adjusted heat capacities below $T_C/2$ and above T_C, the effective Θ_D's for U_3Sb_4 were evaluated and plotted against temperature. The gap in the curve caused by the transition was bridged and converted into a non-cooperative heat capacity. That for U_3As_4 was then calculated by the method of corresponding states [73]. The excess (cooperative) heat capacities were obtained by the subtraction of the respective integrated curves. Cooperative entropy values of 4.15 cal_{th} mol^{-1} K^{-1} for U_3As_4 and 6.60 cal_{th} mol^{-1} K^{-1} for U_3Sb_4 were thus obtained.

Since at the transition temperature essentially only the two lowest singlets are populated, an effective spin (s) equal to 1/2 results. This gives a $\Delta S_{tr} = R \ln(2s + 1) = R \ln 2 = 1.38\,cal_{th}$ (mol U)$^{-1}$ K^{-1}, [74] in good agreement with the experimental value for U_3As_4: $\Delta S_{tr} = 1.4$ cal_{th} (mol U)$^{-1}$ K^{-1}. The ΔS_{tr} for U_3Sb_4 (2.2 cal_{th} mol^{-1} K^{-1}) cannot be explained thus unless the higher excited levels are lower in energy than those for U_3P_4. [63] The reputed presence of conduction electrons in U_3Sb_4, however, has been neglected in the above model.

Since these ΔS_{tr}'s are so much smaller than theoretical values of $\Delta S_{tr} = R \ln(2J + 1) = R \ln 9$ for the $^3H_4$ ground term and since the observed heat capacities at high temperatures are seen to be much larger than would be expected from lattice dilational contributions, additional electronic contributions are to be anticipated.

The lattice heat capacities of U_3As_4 and U_3Sb_4 at constant volume were generated from effective Θ_D values equal to 240 and 190 K, obtained as the maximum values of the adjusted heat capacities below the transition. A dilational contribution $C(d) = C_p - C_v$ was calculated from the Nernst-Lindemann expression $C(d) = AC_p^2(\frac{T}{T_m})$, in which $A = 0.0212$ K mol cal^{-1} and T_m, the melting point of the compounds, is taken to be 1700 K. The quantity $[C_v + C(d)]$ is then subtracted from the observed heat capacity to give the total electronic heat capacity, as shown in Fig. 6. This arises from the cooperative (magnetic) contribution already discussed and the excitation of additional electronic levels. Assuming the energy levels of U_3Sb_4 to be approximately the same as those for U_3P_4, the Schottky heat capacity contribution in the region above T_C can be calculated from the levels and degeneracies given by Troc et al. [63], assuming that the two low levels represent a doubly degenerate level responsible for the cooperative phenomenon. The resulting neat capacity, shown in Fig. 6, is essentially compatible with the high-temperature data, but a better fit may be obtained by lowering some energy values slightly.

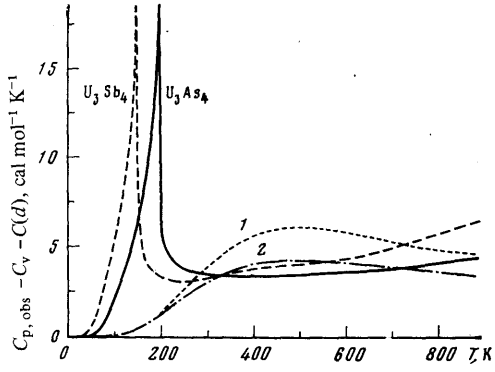


Figure 6. Excess heat capacities $[C_{p,obs} - C_v - C(d)]$ for ferromagnetic transitions in U_3As_4 and U_3Sb_4. The higher-temperature data are fit by a two level Schottky heat capacity contribution using the energies of Troc et al. (– – – – –) [63] and those of the authors (cf. text) (–·–·–). [64]

Entropies of transition significantly below the value expected for the ground-term degeneracy are observed for several uranium compounds [66]. As pointed out by Counsell et al. [75], such low ΔS_{tr} values are evidence of crystal-field effects.

A model that does not require assumptions about a definite ionic state and allows for the essential interdependence of magnetic and conduction phenomena has been proposed by Robinson and Erdös [76]. The model takes into account the closeness of the 5*f*- and the 6*s*-levels of uranium. This model has been successful in explaining the electronic and magnetic transition in UP. The larger ΔS_{tr} for U_3Sb_4 can be explained qualitatively by the fact that U_3Sb_4 is more metallic and has a lower ordering temperature than U_3As_4. This model cannot be applied to U_3As_4, since its resistivity behaviour is very different from that of uranium monopnictides.

UPn_2 compositions. The UPn_2 compositions we have studied are again the arsenide and the antimonide only. These results [77] already published in a concise form will be but briefly mentioned here.

In the dipnictide series UN_2 is an exception; it is stable only under high N_2 pressure and has the fluorite structure [78]. The remaining members UP_2, UAs_2, USb_2, and UBi_2—are isostructural with the tetragonal Cu_2Sb structure. Magnetic susceptibility and neutron diffraction measurements have been made on the four dipnictides from UP_2 to UBi_2. The dependence of the inverse magnetic susceptibility on temperature indicates that all the compounds are ordered antiferromagnetically and that Curie-Weiss behaviour obtains above the ordering (Néel) temperature. The paramagnetic moment increases monotonically with increasing pnigogen size, but Néel temperatures do not. Hence the magnetic coupling may either be anomalously weak, as in UP_2 or anomalously strong, as in UAs_2.

The antiferromagnetic structures of UP_2, UAs_2, and USb_2 determined by neutron diffraction (in the ordered state) consist of ferromagnetic sheets of uranium ions stacked perpendicularly to the c-axis and in the sequence $+ - +$. The magnetic unit cell is twice as large as the chemical one due to its doubled c-axis. In contrast to this, the UBi_2 chemical and magnetic unit cells are identical and the ferromagnetic sheets have the order $+ - + -$. The compounds display metallic conduction with $\rho(298\,K) = 1.83 \times 10^{-4}$ and 1.95×10^{-4} ohm cm for single-crystal samples of UP_2 and UAs_2 respectively[79].

The heat capacity of UP_2 (22.5 to 350 K) has been reported by Stalinski et al.[80] Here a prominent lambda anomaly at 203.2 K accords well with the transition to the antiferromagnetic state, as observed in magnetic susceptibility measurements. In our measurements on UAs_2 and USb_2,[81] we found that both substances show λ-type transitions in the heat capacity with maxima at 272.2 and 202.5 K respectively. Heat capacities below 5 K were extrapolated with a term proportional to T^3 (Debye lattice contribution) and one proportional to T (conduction electron contribution γ). The respective parameters, the Θ_D and γ, were taken from C_p/T versus T^2 plots of the heat capacity below about 20 K. The values of γ were found to be 1.36×10^{-3} cal_{th} mol^{-1} K^{-2} for UAs_2 and USb_2.

Difficulties associated with determination of magnetic heat capacity contributions have been alluded to already and are encountered with uranium compounds involving Group IV, V, and VI elements[66,75]. In the absence of heat-capacity data for the isostructural diamagnetic compounds (i.e. the corresponding thorium compounds) such resolutions must be regarded as tentative and probably too low. It is interesting to note, however, that the heat capacity of USe_2 [82] (with nearly the same molecular weight as UAs_2 although its crystal structure differs) agrees rather well with the heat capacity of the latter compound for some ranges both above and below the transition and with our lattice contribution described below.

The magnetic ordering contributions were determined by plotting the effective Θ_D's for the total heat capacities as a function of T and by interpolating over the gap caused by the enhanced heat capacity in the transition region. The Θ_D's thus obtained over this interval were used to generate "lattice" heat capacities, which were then integrated.

The amount of entropy to be expected is relevant to the interpretation of the ΔS_m, despite reservations about well defined oxidation states for conducting compounds involving the pnigogens. Naively, one may—at least initially—adopt a model with a specified oxidation state for uranium (U^{4+}) and proceed from the free-ion, ground term ($^3H_4$), on the assumption of Russell-Saunders coupling, to the expected magnetic entropy $R \ln(2J + 1) = 4.37$ cal_{th} mol^{-1} K^{-1}. The failure of the experimental results to account for this amount of entropy is usually attributed to the crystal-field quenching of the orbital moment. Occasionally the paramagnetic moment and the excess entropy in such systems can be identified more closely with spin-only values, which in the present case would be $R \ln(2S + 1) = R \ln 3 = 2.18$ cal_{th} mol^{-1} K^{-1}. The paramagnetic moments are all less than the free-ion values (3.58 μ_B) and vary from below the spin-only value (2.83 μ_B) for UP_2 to near the free-ion value for UBi_2. However, $\Delta S_m(UAs_2) = 0.99$ cal_{th} mol^{-1} K^{-1} and $\Delta S_m(USb_2) = 1.70$ cal_{th} mol^{-1} K^{-1} are both well below even the spin-only values.

The UP_2 heat capacity near 350 K is already well above the Dulong and Petit limit and the trend of these data contrasts markedly with that for UAs_2 and USb_2. Magnetic susceptibility[83], electrical conductivity[84], and more recently X-ray crystallographic[85,86] studies have shown the presence of a phase transition in UP_2 near 356 K, where the tetragonal superstructure disappears on heating.

X. THE COPPER–SULPHUR SYSTEM

Although early investigations indicated that the copper–sulphur system is relatively uncomplicated and consists, in fact, of only three binary phases, covellite (CuS), digenite ($Cu_{1.80}S$), and chalcocite (Cu_2S), recent studies have produced a veritable population explosion of distinct new phases in the system, which have not as yet yielded an unambiguous phase diagram, particularly in the region below 400 K. The marked ambiguity is produced by a multiplicity of phases, a strong tendency of the copper–sulphur system to exhibit metastability, and confusion—partly because of the similarity—of the X-ray diffraction patterns and optical properties. Moreover, extensive solid solutions, unquenchable phases, and phase transformations produced by grinding and handling have created considerable confusion since the comprehensive study of the phase equilibria in this system by Roseboom[87]. Since this almost classical study, numerous additional papers have appeared reporting the application of a great variety of techniques. Perhaps one of the most interesting, from the point of view of a thermodynamicist, is one as yet not in print, by R. W. Potter[88], in which he has been able to resolve much of the contradictory nature of the other data by means of galvanic cell measurements to delineate the metastable equilibria, the stable phase diagram, and the thermochemical properties of both phases.

We may note that, like the first system mentioned in this paper, the present one, the last to be discussed, is mineralogical. However, marcasite is already known in the literature, whereas our data on the copper–sulphur system are the least complete of any that I have discussed today and work is still, therefore, in very active progress. We are eager to obtain thermophysical data to test the correctness of Potter's galvanic cell studies[88].

To date, we have studied the high- and low-temperature heat capacities of the three copper compositions which I mentioned as those originally identified with the system. We are undertaking measurements at the present time on anilite and djurleite.

One of the remarkable aspects of the behaviour of these materials is in the fact that, under some temperature conditions, many of them show "superionic conductivity" to an interesting degree.

Turning our attention to digenite, we note first of all that at about 350 K high-temperature digenite transforms on cooling into low-temperature digenite. Rather more amazing is the fact that at 310.8 K—just above room temperature—a transition occurs which we are obliged to describe as a disproportionation transition. Apparently, on cooling to about this temperature, one departs from the solid-solution range of the low-temperature digenite phase and crosses the boundary into the low-temperature digenite–djurleite field. In other words, the low-temperature digenite disproportionates to some extent into djurleite. Although one is inclined to think of disproportionation equilibria as relatively slow phenomena even at elevated temperatures, there is nothing very slow about this transition. It should be noted, of course, by examining the

phase diagram[87,89], that the boundary mentioned above apparently continues to be a function of temperature well below 300 K.

It appears that the transformation takes place gradually as one goes down in temperature and our measurements indicate that it is insufficient to supercool 10 or 20 K below the above transition; one has to go to very low temperatures indeed if a reproducible enthalpy of disproportionation is sought. As a matter of fact, we found it routinely most convenient to cool a full 100 K below the transition in order to ensure a complete transformation. The exact trend of the boundary between the fields is apparently not yet well delineated, but we find that we can reproduce to within approximately 0.01 per cent the enthalpy increment associated with this transition. The overall shape of the transition is presented in Fig. 7. The dashed lines represent an interim estimate of the lattice contribution, which will probably ultimately need revision[90].

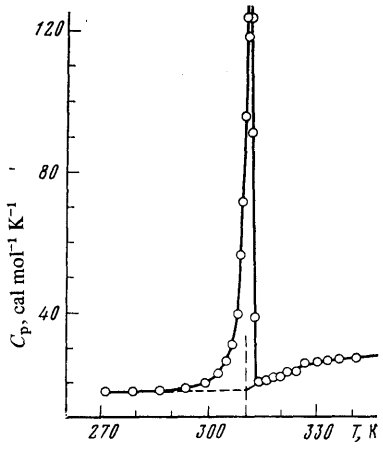


Figure 7. The heat capacity and disproportionation anomaly in lowdigenite $Cu_{1.80}S$.[90]

The enthalpy increment of this transition (ΔH_{tr}) is 477 cal$_{th}$ K^{-1} and the corresponding entropy is 1.50 cal$_{th}$ mol^{-1} K^{-1} or just slightly larger than $R \ln 2 = 1.38$ cal$_{th}$ mol^{-1} K^{-1}. In all respects this has proven to be one of the most striking disproportionation transitions ever encountered in that the rapidity with which equilibrium is reached is unusual. A detailed analysis of the heat-capacity curve below the transition has not yet been completed but it will presumably show excess heat capacity for a gradual transformation of the sample with temperature.

It has been my pleasure to summarize for you some of the recent types of phenomena we have been encountering in the heat-capacity studies in recent months in both the chalcogenides and the pnictides. Were greater time available, more examples could have been discussed and presented and would have shown an even greater diversity. We have not yet reached the point where we recognize anything which can be described as "typical behaviour" and find rather a very interesting variety of phenomena.

There still remains a great deal more of "systematic" work to be done. Table 2 does summarize the thermophysical functions which have become available as a result of our studies on the compounds mentioned in this presentation.

Table 2. Thermodynamic functions for chalcogenides and pnictides at 298.15 K recently determined by Grønvold and Westrum et al.

Substance	S°, cal mol^{-1} K^{-1}	$H^\circ - H^\circ_0$, cal mol^{-1}	$-[(G^\circ - H^\circ_0)/T]$ cal mol^{-1} K^{-1}
	Chalcogenides		
FeS_2 (marcasite)	12.88	2328	5.07
$CoSe_2$	23.10	3543	11.21
$CoTe_2$	27.37	3889	14.32
CuS	—	—	—
$Cu_{1.80}S$	—	—	—
Cu_2S	—	—	—
	Pnictides		
$FeSb_2$	25.98	3905	12.88
$CrSb_2$	27.46	4009	14.01
CrAs	15.40	2506	6.99
UAs_2	29.41	4282	15.05
U_3As_2	73.87	10405	38.97
USb_2	33.81	4596	18.39
U_3Sb_4	83.60	10943	46.89

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Department of Chemistry,
University of Michigan,
Ann Arbor, Michigan 48109,
U.S.A.