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HEAT CAPACITIES IN CRITICAL REGIONS

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Abstract—In this paper available heat capacity results in the liquid–gas, and the magnetically critical regions are referenced and discussed. Emphasis is placed on cases where critical exponents have been evaluated and they are compared with theoretical predictions.

I. INTRODUCTION

Critical phenomena and phase transitions have been intensively studied from several points of view, and many comprehensive accounts have been published in recent years.[1–12] The enormous interest in the thermodynamic singularities and spatial correlations associated with higher order transitions stems partly from the wish to explore the relationships and possible equalities of different types of transitions in order to find more unifying concepts. In other cases the prime interest has been the entropy or enthalpy increments of transition. Also in these cases a closer examination might be rewarding, but it is deplorable that often, good experimental heat capacity results are neither given explicitly nor in another form that permits others to extract or re-evaluate critical exponents.

Classical theories like that of van der Waals for the liquid–gas behavior, the Bragg–Williams–Bethe theory for structural order-disorder, the Weiss molecular field theory for magnets, and the Landau universal theory of critical phenomena, all predict increasing but finite heat capacities as the critical temperature (T_c) is approached from below, and a discontinuous heat capacity decrease—heat capacity drop—as T_c is exceeded. In the cases of both structural and magnetic transitions the excess heat capacity should be zero above T_c according to the classical theory. The incorrectness of the Landau theory for an exactly soluble case was proved by Onsager[13] in 1944, and since that time a growing amount of experimental and theoretical work has substantiated the common occurrence of non-classical behavior in critical regions.

Indications of fundamental similarities in heat capacity and other property behavior between seemingly very different phase transitions are often encountered. Thus, the heat capacity behavior of carbon dioxide in the liquid–gas critical region resembles that of the structural order–disorder transformation in β-brass, and that of europium monosulfide in the region of its change from ferro- to paramagnetism.

The heat capacity is one of the most difficult properties to analyze in the critical regions because of its slight divergence. In addition, the heat capacity peak is often somewhat rounded from crystal imperfection and possible other causes. Furthermore, the difficult question of how far the critical region extends also needs to be answered. In this survey attention will be focussed on heat capacity data of such accuracy that analysis of critical behaviour has been or can be performed with reasonable success. An analysis of this nature has been made by Cook[8] on 24 magnetic solids on the basis of available data. More recent analyses will also be considered here, and the analysis will be extended to other magnetic compounds and to some transitions of other kinds, in order that similarities might be exposed.

After some comments about the methods used for heat capacity determinations in critical regions and the analysis of critical data, the heat capacity behavior of different categories of transition will be considered, starting with the liquid–gas case. A substantial amount of accurate heat capacity data is available for this classical case, and also for the different alternatives of cooperation in magnetic systems. A considerable number of systems have been carefully investigated and some of them already analyzed in terms of critical exponents etc. Time does not permit coverage of other types of transition and they will only be mentioned here. The well-known structural order–disorder transformations are not easily categorized, and have been analyzed only in a few cases. Even when they are not coupled with magnetic or electrical changes the continuity might be forbidden by symmetry, and a first order component comes into play. The very extensive heat capacity data on orientational phase changes in molecular solids has been treated by others and will not be covered in this short survey.

The closure of liquid and solid miscibility gaps presents a less closely studied case which shall need future attention.

Ferro- and anti-ferroelectric transitions have been extensively studied by many methods, yet sufficiently accurate critical temperature heat capacity data are only now appearing. This stems from the fact that the transformation is more 'classical' in nature and that the critical region is rather narrow due to the smoothly decaying coulombic force.

An even more narrow critical region is expected for the superconductors due to the very long coherence length. Finally, the solid–liquid phase change will be mentioned, as it also might show a kind of critical behavior as the fusion temperature is approached.

II. CALORIMETRIC TECHNIQUES AND ANALYSIS OF CRITICAL DATA

1. *Heat capacity determinations*

The present survey is not particularly concerned with the experimental techniques of obtaining heat capacity data, but some comments might be in place since the different methods to some extent seem to give different results.

In the usual absolute methods the energy supplied to the system and the temperature rise of the system form the basic data for deducing the heat capacity of the sample as a function of temperature. Measurements are usually performed for rising temperatures only. In the low temperature region the temperature of the surrounding shield is often kept constant during an experiment (isothermal shield calorimetry) while for higher temperatures the shield temperature is generally regulated as to follow that of the calorimeter surface (adiabatic shield

calorimetry). These methods are discussed in every detail in *Experimental Thermodynamics.*[14]

For measurements in the liquid–gas critical region the sample height needs to be small in order that the rounding of the peak due to gravitational effects be minimized.[15] In some cases the fluid is stirred during the experiments. This upsets the effect of gravity and tends to minimize the temperature gradients in the sample, but it might conceivably influence the critical behavior.

The temperature increments used in the determination of heat capacity must be suitably small compared to $(T - T_c)$ or the resulting heat capacity must be corrected for curvature in the critical region. The heat capacity divergence is usually small and it is estimated[3] that it suffices to keep $\Delta T < |T - T_c|/3$.

Another type of experimental method, which is known as the AC-method, has been used in many recent studies where exponents have been reported. Developed and described by Kraftmakher,[16] Sullivan and Seidel[17,18] and others, its characteristic feature is the transfer of energy pulses to the sample and measurement of the temperature variation as a function of temperature. Kraftmakher and Romashina[19] heated their iron sample by direct current and superposed a 30 Hz alternating current. Handler *et al.*[20] kept their thin nickel foil sample in an electrically heated furnace and used chopped light pulses from a tungsten lamp for providing the extra energy, see Fig. 1. The amplitude of the temperature fluctuations of the sample was measured by a phase-sensitive lock-in amplifier, and the output taken as inversely proportional to the heat capacity. The results were then normalized on the basis of available heat capacity data for nickel.

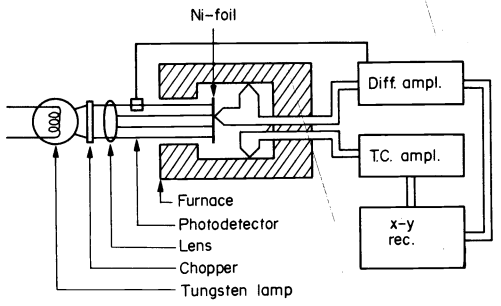

Fig. 1. Principle of AC-calorimetry.[20]

Two time constants are of prime importance in this type of experiment, viz (1) the thermal relaxation constant of the sample, and (2) that between sample and surrounding, which is generally much larger than that of the sample. The thermocouple lag is considered negligible due to the smallness of the spot-welded thermocouple junction. Even though the increasing sample relaxation time might be accounted for, the nature of the measurements is different from that of ordinary calorimetry with temperature equilibration between inputs. Since the attainment of thermodynamic equilibrium in a sample might take hours in the critical region, sufficient time has not in many cases been provided. The results might then be unreliable for analyzing the critical behavior.

2. *Critical analysis*

Heat capacities in a critical region are usually analyzed in terms of critical-point exponents which describe the behavior of a function $f(\epsilon)$ in the region of interest. The parameter ϵ is defined as

$$\epsilon = \frac{|T - T_c|}{T_c}$$

and is a reduced temperature increment or decrement from the critical temperature. We are interested in a possible limiting value α

$$\alpha = \lim \frac{\ln f(\epsilon)}{\ln \epsilon}, \quad \text{when} \quad \epsilon \to 0$$

and call it the critical exponent. The actual function is unknown in most cases, but based on the solution of the two dimensional Ising model the following function is often used in the analysis:[4,5]

$$C = \frac{A'}{\alpha'}(\epsilon^{-\alpha'} - 1) + B' \quad \text{for} \quad T < T_c,$$

and

$$C = \frac{A}{\alpha}(\epsilon^{-\alpha} - 1) + B \qquad \text{for} \quad T > T_c.$$

The two-dimensional Ising model expression

$$C = -A \ln \epsilon + B$$

then results for $\alpha = 0$. For the latter alternative the experimental data might be analyzed by plotting the transitional heat capacity against $\log |T - T_c|/T_c$ in the region below and above the critical temperature. Straight lines indicate that $\alpha' = \alpha = 0$, and parallel lines that $A' = A$. In case of curvature one might replot the data as $\log C$ against $\log |T - T_c|/T_c$. Straight line relationships give the critical exponents which can be positive, zero, or negative.

For the simple functional relationship defined above $\alpha = 0$ means logarithmic divergence, but other functional relationships for $\alpha = 0$ might correspond to a cusp-like singularity (or to an analytical function with a discontinuity jump).

The scaling hypothesis predicts that $\alpha' = \alpha$ and $B' = B$, while in general $A' \neq A$. Thus, a plot of $\log C$ against $\log \epsilon$ should be asymptotically linear (asymptotic scaling) with equal slopes for the branches above and below T_c.

This equality holds over decades in some cases but not in others. Further terms can, however be included in the scaling process to cover a larger range of ϵ (extended scaling). For example[21,22]

$$C = \frac{A}{\alpha}(\epsilon^{-\alpha} - 1)(1 + D\epsilon^x) + B + E\epsilon.$$

It is assumed that $x > 0$ so that the term $D\epsilon^x$ represents a singular term which vanishes at T_c and is of higher order than the leading singularity $(A/\alpha)\epsilon^{-\alpha}$.

Various methods have been used for fitting experimental data to the above functions and related ones[8,22–24] and those for the various compounds for which critical exponents have been determined.

The derived α-values are influenced by the various constraints laid on the coefficients and are presumably more uncertain than the standard deviations might indicate. Furthermore, they depend on the range of ϵ chosen, as in many cases the linearity is limited to one or two decades in ϵ only.

According to the universality hypothesis[25] the critical exponents do not change as long as the dimensionality (d) and the effective number of degrees-of-freedom (n) re-

main unaltered. Thus, for a magnetic system the critical exponents should not vary with the value of the spin quantum number or the exchange parameter values as long as the nature of the system remains unchanged.

Among cases with one degree-of-freedom ($n = 1$) are the liquid–gas system, the Ising (1/2) system, and structural order–disorder systems of the β-brass type. With the superfluidity transition in liquid helium with $n = 2$, while, as expected, magnetic systems with isotropic interactions have $n = 3$, which also corresponds to the physical dimensionality of the system ($d = 3$).

The universality hypothesis does not predict numerical values for critical exponents. They have been exactly determined in three dimensions for rather special cases only. Most of the physically interesting values have come from series expansion work, and more recently from renormalization group technique. Some results are listed in Table 1.

Table 1. Calculated critical point exponents for heat capacity

Lattice dimens.	Degrees-of-freedom	α'	α	Ref.
$d = 3$	$n = 1$ (Ising)		1/8	26–30
		$0.066 < {}^{+0.16}_{-0.04}$		31
		1/8		28, 32
		0†		32
	$n = 2$ (planar)	~0	~0	33, 34
	$n = 3$ (Heisenberg)		-0.2 ± 0.05	35
			$-1/8 - -1/16$	36
			-0.14 ± 0.06	37
		$\sim -1/10$	$\sim -1/10$	34
	$n \to \infty$ (spherical)	−1	−1	34
$d = 2$	$n = 1$ (Ising)	0	0	13

†For $\epsilon > 10^{-4}$.

III. TRANSITIONS

1. *Liquid–gas transitions*

In the century that has passed since Andrews observed critical behavior in carbon dioxide, a wealth of information about liquid vapor behavior has been accumulated. If we look at the familiar p-T diagram for carbon dioxide, see Fig. 2, we note the disappearance of the liquid–gas coexistence curve above the critical 'point' 304.2 K and 78 atm. Similarly, the densities of the coexisting liquid and gas phase approach each other as the temperature is raised and become equal at the critical 'point'. The existence of a quantity which is different from zero below the critical temperature and zero above is a useful characteristic. For the liquid–gas case the difference in density between liquid and gas $d(l) - d(g)$ can be taken as the order parameter of the critical system.

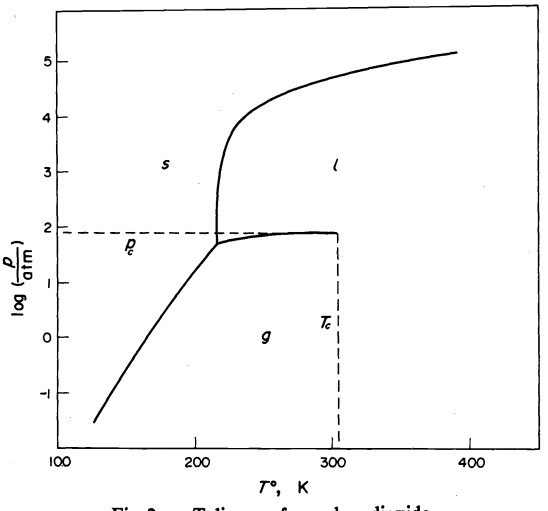

Fig. 2. p-T diagram for carbon dioxide.

In 1945 Guggenheim[38] normalized the liquid vapor density difference vs T/T_c for eight simple fluids (Ne, Ar, Kr, Xe, N_2, O_2, CO, and CH_4) and showed that the curves practically coincided. Another feature of this best-fit to the data—or corresponding states curve—was its lack of compliance to the quadratic function predicted by the Van der Waals theory. The best-fit is rather of the cubic type corresponding to $d - d_c \propto (|T_c - T1/T_c)^\beta$ with $\beta = 1/3$. For some time it was thought that $\beta = 1/3$ was a universal exponent valid also for other critical phenomena, but this idea was soon abandoned.

A related behavior is apparent for heat capacities in the critical region. Until rather recently it was not clear if the divergence was limited to the constant pressure heat capacity while C_V remained more or less unaffected. However, the first really accurate heat capacity determinations by Bagatskii *et al.*[39] on argon in the liquid–gas region for $V \approx V_c$ suggested that C_V also tends to high values as the critical temperature is approached from either side.

The precise measurements were soon extended to oxygen by Voronel *et al.*[40] and also in this case the results were interpreted in terms of a logarithmic divergence (see Table 2). Moldover and Little[41] obtained heat capacity results in the critical region for ^{3}He and ^{4}He and interpreted them similarly in terms of logarithmic divergence. In the meantime Fischer[42] had made an approximate calculation for the three-dimensional Ising model and reanalyzed the argon[39] and oxygen[40] data in terms of $C_V \propto (T - T_c)^{-\alpha}$ with a small positive value of $\alpha \approx 1/5$. Moldover and Little[41] judged that the accuracy of their data did not permit one to distinguish between the two alternatives. More recent work on ^{4}He by Moldover[45] gave $\alpha' = \alpha = 0.15$, while that on ^{3}He by Brown and Meyer[43] resulted in $\alpha' = \alpha = 0.105$.

Voronel *et al.*[46] redetermined the heat capacity of argon under conditions closer to critical density than in the earlier work, and tried to analyse the results in terms of a power law dependence in accordance with a suggestion by Fischer.[42] Above T_c they found that the power law with $\alpha \approx 1/4$ and the logarithmic divergence accorded equally well with the results, but favored the latter. Further improved measurements by Voronel *et al.*[47] on argon and methane led to the conclusion that the critical exponents had the same value ($\alpha' = \alpha = 1/8$) below and above the critical temperature, and were equal for the two fluids.

The first measurements by Voronel *et al.*[48] on xenon and the heat capacities derived by Schmidt *et al.*[49] from ice calorimetric experiments were not accurate enough for determining the value of this critical exponent. Later work by Edwards *et al.*[50] resulted in $\alpha' = \alpha = 0.08$ but other values from 0 to 1/8 could not be ruled out.

Only a few heat capacity studies of heteroatomic molecules have been carried out in the critical region. In a recent study of water ($T_c = 647.3$°K, $P_c = 218.2$ atm) by Baehr[51] and Baehr and Schomäcker[52] several isochores were studied, but the character of the singularity could not be deduced because of uncertainty about the influence of gravity. Earlier measurements by Amirchanoff and

Table 2. Critical exponent data for liquid–gas transitions

Substance	Authors	Year	T_c/K	Crit. exponent α'	Crit. exponent α	Evaluator
^3He	Moldover and Little[41]	1965		0	0	
	Brown and Meyer[43]	1972	3.3092 ± 0.0001	0.105 ± 0.015	0.105 ± 0.015	
^4He	Moldover and Little[41]	1965		0	0	
				0.07 ± 0.04	0.07 ± 0.04	Vincentini-Missoni *et al.*[44]
	Moldover[45]	1969	5.1891 ± 0.0007	0.15	0.15	
Ar	Bagatski *et al.*[39]	1962	150.5	0	0	
	Voronel *et al.*[46]	1965		<0.25	<0.25	Kadanoff *et al.*[4]
				<0.4	<0.4	
	Voronel *et al.*[47]	1972	150.663_3	0.125	0.125	
Xe	Voronel[48]	1961		<0.2 ± 0.1	<0.2 ± 0.1	Kadanoff *et al.*[4]
	Schmidt *et al.*[49]	1967	289.42			
	Edwards *et al.*[50]	1968	289.697	~0.08	~0.08	
				0.065	0.065	Vincentini-Missoni *et al.*[44]
O_2	Voronel *et al.*[40]	1963	154.565	0	0	
				<0.25	<0.25	Kadanoff *et al.*[4]
				<0.4	<0.4	
CO_2	Michels and Strijland[56]	1952		<0.1 ± 0.5	<0.1 ± 0.5	Kadanoff *et al.*[4]
	Lipa *et al.*[57]	1970	303.925 ± 0.005	0.125 ± 0.01	0.125 ± 0.01	
C_2H_6	Voronel *et al.*[47]	1972	305.362_7	0.125	0.125	

Kerimoff[53] and Kerimoff[54] were also unsuited for such deduction according to Levelt Sengers and Greer.[55]

The early measurements on carbon dioxide by Michels and Strijland[56] clearly showed non-classical behavior. Critical exponents were deduced by Lipa *et al.*[57] and Buckingham[58] from heat capacity measurements on a one millimeter high sample of CO_2 at temperatures to within 12 mK of its critical temperature. The resulting exponents were $\alpha' = \alpha = 0.125 \pm 0.01$.

Studies of critical behavior in fluid mixtures are still scarce. Chaskin *et al.*[59] measured the constant volume heat capacity of air and of impure nitrogen (0.7% O_2 and ~0.5% Ar). In addition to the λ-type maximum they found a second discontinuity occurred as the heat capacity decreased with increasing temperature above the maximum.

Brown and Meyer,[60] motivated by the extension of critical region theory to binary systems by Griffiths and Wheeler,[61] carried out measurements on a 4:1 ^3He:^4He mixture in the vicinity of the liquid–gas critical point. A weak divergency characterized by $\alpha \sim 0.1$ was observed, but it was judged not to correspond to really asymptotic behavior.

To conclude this section, all the more recent critical exponent determinations in the liquid–gas critical region conform well with the scaling prediction $\alpha' = \alpha$. The values found for the exponents are rather close to 1/8, the value derived theoretically for the three-dimensional Ising model.

2. *Superfluidity transitions*

The commonly called λ-type heat capacity behavior which we have been discussing for the liquid–gas critical region was first observed for liquid helium in its superfluidity region by Keesom and Clusius.[62] After the more extensive measurements by Keesom and Keesom[63] it was generally supposed that the λ-transition in ^4He was of second order in the Ehrenfest[64] classification, that is finite and discontinuous. In contrast to this, accurate heat capacity measurements by Fairbank *et al.*[65] and Buckingham and Fairbank[66] to $|T - T_\lambda| = 10^{-6}$ indicated a logarithmic singularity. Similar conclusions were arrived at by Lounasmaa and Kojo[67] and McCoy and Graf.[68]

As result of extensive heat capacity measurements Ahlers[21,69–71] also found that the critical exponents α' and α were near zero. The ratio A/A' was greater than unity, however, and pressure dependent. These results are inconsistent with the Widom,[72,73] Domb and Hunter,[27] Kadanoff[74] scaling predictions, and even after including singular higher order terms Ahlers found it virtually impossible to interpret the measurements consistent with scaling and $\alpha' = \alpha = 0$. He then assumed that $\alpha' = \alpha \approx 0$ and tried to fit the data to the equation

$$C_p = \frac{A}{\alpha}(\epsilon^{-\alpha} - 1)(1 + D\epsilon^x) + B.$$

If $x' = x = 0.5$, in accordance with theory, consistency with the measurements was obtained with slightly negative values of α' and α ($\alpha' = \alpha = -0.02 \pm 0.02$).

The heat capacity determinations of ^3He–^4He mixtures in the λ-transition region by Gasparini and Moldover[75] extended the earlier work by de Bruyn Ouboter *et al.*[76] to temperatures much closer to the λ-line. The data for pure ^4He confirmed the earlier reported symmetrical logarithmic divergence, but the singularity, although sharp, became less prominent as the mole fraction of ^3He increased from 0.0110 to 0.390. The results support the conjecture[77] that the heat capacity of the mixtures at constant chemical potential becomes infinite at the λ-line for all concentrations of ^3He.

3. *Magnetic transitions*

It has been known for at least 150 yr that iron,† cobalt

†According to Barlow[78] it is stated in Newton's Optiks that red-hot iron has no magnetic property, but this observation remained controversial for a long time.

and nickel lose their ferromagnetic properties on heating to a characteristic temperature and regain them on cooling.[78–80]

The thermal phenomenon accompanying the magnetic transition in these metals was apparently first studied by Pionchon,[81] who found that the heat capacities increased markedly in the range up to where the change in magnetic state occurred. According to Weiss and Beck[82] the magnetic heat capacity of iron, nickel and magnetite (Fe_3O_4) increases with temperature and drops abruptly to zero at a given temperature (the Curie temperature) in accordance with the Weiss molecular field theory,[83] see Fig. 3. More recent measurements on magnetite[130] show a more pronounced maximum, see Fig. 3. Related thermal observations for another class of magnetic materials, the antiferromagnets, date back to the results by Millar[84] on MnO in 1928, which clearly showed non-classical behavior.

The literature on heat capacities in transition regions is difficult to encompass and the author apologises for not having covered it completely. Even so, a partial list of substances studied by various investigators might be of use and is provided in Tables 3 and 4.

In discussing the thermal aspects of the cooperative magnetic transitions, we shall first consider the substances with permanent magnetic moment at low temperatures—the ferro- and ferrimagnets—and then the antiferromagnets. Both will be considered according to substance classes: metals, halides, chalcogenides, pnictides and misc.

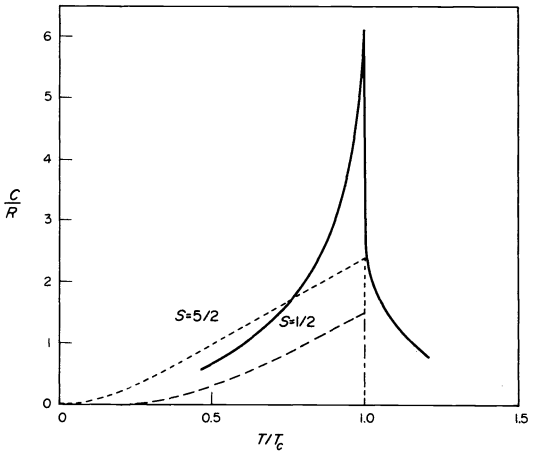

Fig. 3. Magnetic heat capacity according to the molecular field theory for $S=\frac{1}{2}$ and $S=\frac{5}{2}$, and the actual behavior of the ferrimagnet Fe_3O_4.[130]

a. *Ferro- and ferrimagnetic substances*

Metals. The heat capacity study of iron by Kraftmakher and Romashina[19] was prompted by the previously observed logarithmic nature of the temperature dependence in the liquid–gas critical region. The heat capacity was measured by an AC-modulation method in the temperature range 950–1200 K and correspondence with logarithmic behavior noted over the range 10^{-1}–10^{-3} in ϵ. More

Table 3. Heat capacity data on ferro- and ferrimagnetic substances in the critical region

Substance	T_c/K	Ref.	Substance	T_c/K	Ref.
Metals			Pnictides		
Fe	1043	19, 82, 85–96	CrAs	265	142
Co	1403	97–100	MnAs	316	143–149
Ni	631	20, 101–111	$Mn_{2.10}Sb$	552.2	150
Eu	16.5	112, 113	Mn_2Sb	546.5	150
Gd	289	114–117	$Mn_{0.98}Sb$	580	151
Tb	227.7	118a, 118b	NdN	27.6	152
Dy	83.5	119	GdN	69; 67.4	153, 154
Ho	19.4; 17.5; 16	120–122	TbN	33.7	154
Er	19.9	123	HoN	13.3	154
Fe–Cr		96	DyN	17.6	154
Pd–Mn		124	ErN	3.39	154, 155
			$UN_{1.59}$	94	156
Hydrides			$UP_{1.35}$	136.5	157
β-UH_3	170.7	125	$UAs_{1.33}$	196.1	142
			$USb_{1.33}$	147.5	142
Halides			Misc.		
$K_2CuCl_4 \cdot 2H_2O$	0.88	126, 127	$Mn(CH_3COO)_2 \cdot 4H_2O$	3.18	158
$(NH_4)_2CuCl_4 \cdot 2H_2O$	0.70	126, 127	$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.176	159
$Rb_2CuCl_4 \cdot 2H_2O$	1.02	127	$MnFe_2O_4$	287	160
$(NH_4)_2CuBr_4 \cdot 2H_2O$	1.73	127	$Zn_{0.38}Mn_{0.62}Fe_2O_4$	447	161
$LiTbF_4$	2.885	24	$Zn_{0.5}Ni_{0.5}Fe_2O_4$	583	161
			$Zn_{0.5}Mg_{0.5}Fe_2O_4$		162
Chalcogenides			$Ni_3La_2(NO_3)_{12} \cdot 24H_2O$	0.393	163
Cr_5Te_6	327	128	$Dy(C_2H_5SO_4) \cdot 9H_2O$	0.115	164
Cr_3Te_4	300	128	US–UP		165
Cr_2Te_3	172	128	UOTe	162	166
Fe_3O_4	848.5	82, 85, 129, 130			
Fe_7Se_8	451	131			
Fe_3Se_4	307	132			
EuO	69.31	133–137			
EuS	16.2	138, 139			
US	180.1	140			
USe	160.5	141			

Table 4. Heat capacity data on antiferromagnetic substances in the critical region

Substance	T_c/K	Ref.	Substance	T_c/K	Ref.
	Metals		MnO_2	92.12	84, 223
Cr	311	167, 168	MnS	140; 152	224, 225
α-Mn	95	169, 170	MnS_2	47.93	226
Nd	7.43; 19.55	171, 172a	MnSe	247	142, 227
Sm	13.3	172b, 172c	$MnSe_2$	47.7	142
Eu	88.35	112, 113	MnTe	307	226–229
Dy	174.6	113, 173	$MnTe_2$	83.0	226
Tm	55.5	174	$Fe_{1-x}O$	184; 188.5	221, 230
Ho	131.6	120	Fe_2O_3	955	231–233
	Halides		FeS	590	234
VCl_3	104.9	175	Fe_7S_8	590	234
$CrCl_2$	16.06	176	CoO	287.3	228, 235–237
MnF_2	66.5	177, 178	NiO	522.7	228, 238–240
$KMnF_3$	87.6	179	EuSe	4.58	241, 242
$RbMnF_3$	83.0	22, 180, 181	EuTe	9.64	241
$MnCl_2$	1.81; 1.96	182–188	Er_2O_3	3.3707	243
$MnCl_2·4H_2O$	1.62	189, 190	UO_2	30.44	244, 245
$CsMnCl_3·2H_2O$	4.885	191	USe_2	13.1	246
$MnBr_2$	2.16	192	NpO_2	25.3	247
$MnBr·4H_2O$	2.136	193		Pnictides	
FeF_2	78.3	194–196	CrSb	685	240
FeF_3	367	197	$CrSb_2$	274.0	142
$FeCl_2$	23.7	198, 199	SmN	18.2	154
$FeBr_2$	14.2	199	ErAs	2.84; 3.03	248
CoF_2	37.70	200	ErSb	3.46; 3.51	248
$CoCl_2$	24.71	184	$UN_{1.01}$	52	156, 249
$CoCl_2·2H_2O$	17.20	201	$UP_{1.00}$	22.5; 121	157
$CoCl_2·6H_2O$	2.2890	202–204	UP_2	203.2	250
Rb_3CoCl_5	1.14	205	UAs_2	272.2	142
Cs_3CoCl_5	0.523	164, 206	USb_2	202.5	142
$Cs_3Co_xZn_{1-x}Cl_5$		207		Misc.	
$CoBr_2·6H_2O$	3.150	208	$Mn_3La_2(NO_3)_{12}·24H_2O$	0.230	163
Cs_3CoBr_5	0.282	205, 206	$K_3Fe(CN)_6$	13	251
NiF_2	73.22	209	$FeTiO_3$	57	252
$NiCl_2$	52.35	210	$ZnFeO_4$	9.5	253
$CuF_2·2H_2O$	10.90	211	$Co_3La_2(NO_3)_{12}·24H_2O$	0.189	163
$CuCl_2$	23.91	176	$Ni(IO_3)_2·2H_2O$	2.97	254
$CuCl_2·2H_2O$	4.33	211, 212	$Cu_3La_2(NO_3)_{12}·24H_2O$	0.089	163
$LiCuCl_3·2H_2O$	4.45	211	CeB_6	~10	255
K_3MoCl_6	4.65; 6.55	213, 214	NdB_6	7.5	255
$PrCl_3$	0.4	215	GdB_6	~10	255
$GdCl_3·6H_2O$	0.185	164, 216	$GdAlO_3$	3.69	256
$ErCl_3·6H_2O$	0.356	217	$TbAlO_3$	3.95	256
UI_3	2.61	218	$DyAlO_3$	3.52	256
	Chalcogenides		$GdVO_4$	2.50	257
Cr_2O_3	305	219, 220	$DyPO_4$	3.39	258
MnO	116; 117.8	84, 221	$Dy_3Al_5O_{12}$	2.54	259–261
Mn_2O_3	79.4	222	YbO_2S	2.575	262

recent measurements by MacInnes and Schröder[96] using a pulse heating technique[263] resulted in a negative value of the exponent α' below the critical temperature and a positive value above (Table 5) indicating that there is no basic symmetry in the singularity about the critical temperature. This is at variance with the scaling hypothesis, but such results have been found in many cases where the simple approximation $C = (A/\alpha)(\epsilon^{-\alpha} - 1) + B$ has been used.

The AC-method for heat capacity determinations was also used by Lederman *et al.*[23] for obtaining new results for iron in the critical region. A detailed analysis of the data showed that $\alpha' \approx \alpha$, and the resulting values were $\alpha' = \alpha = -0.120 \pm 0.001$, in excellent agreement with the renormalization-group technique result $\alpha' = \alpha \approx -0.10$ for Heisenberg magnetic systems with isotropic short-range interactions ($d = n = 3$). A reanalysis by Kornblit and Ahlers[137] gave $\alpha' = \alpha = -0.096 \pm 0.023$.

For nickel a similar development in knowledge of critical exponent values is seen to have taken place. Here again the evaluation by Handler *et al.*[20] and by Maher and McCormick[109] indicated negative α' values below the critical temperature and positive above, while the results by Connelly *et al.*[110] and the revaluation by Cook[8] and Lederman *et al.*[23] and Kornblit and Ahlers[137] as well as the results by Major *et al.*[111] all indicate that $\alpha' = \alpha \approx -0.10$.

From the heat capacity measurements on gadolinium by Griffel *et al.*[114] critical exponents were evaluated by Cook,[8] see Table 5. By AC-calorimetry Lewis[115] also found the exponent α to be negative, not only below the transition, but also above. Robinson and Milstein[116] studied the heat capacity behavior with 0.04–1.0 wt % carbon added as impurity, using differential scanning calorimetry. With increasing impurity concentration the peak was lowered and the slope of the steepest portion of the curve was

Table 5. Critical exponent data for ferro- and ferrimagnetic substances

Substance	Authors	Year	T_c/K	Crit. exp. α'	Crit. exp. α	Evaluator
Fe	Kraftmakher and Romashina[19]	1965	1042	0	0	
	MacInnes and Schröder[96]	1970	1044.39 ± 0.14	−0.21 ± 0.04	0.115 ± 0.020	
	Lederman *et al.*[23]	1974	1041.32	−0.120 ± 0.01	−0.120 ± 0.01	Kornblit and Ahlers[137]
				−0.096 ± 0.023	−0.096 ± 0.023	
Ni	Kraftmakher[108]	1965	630	0	0	
	Handler *et al.*[20]	1967	625	−0.3 ± 0.1	0.0 ± 0.1	
	Maher and McCormick[109]	1969	629.635	−0.26 ± 0.06	0.10 ± 0.05	
	Connelly *et al.*[110]	1969	(631.55)	−0.11 ± 0.03	−0.11 ± 0.03	
			631.55	−0.11 ± 0.03	−0.14 ± 0.03	Cook[8]
	Connelly *et al.*[110]	1971	631.58	−0.10 ± 0.03	−0.10 ± 0.03	
			631.58	−0.10 ± 0.03	−0.10 ± 0.03	Lederman *et al.*[23]
				−0.089 ± 0.004	−0.089 ± 0.004	Kornblit and Ahlers[137]
	Major *et al.*[111]			−0.12 ± 0.03	−0.12 ± 0.03	
Gd	Griffel *et al.*[114]	1954		−0.24 ± 0.07	0.11 ± 0.01	Cook[8]
	Lewis[115]	1970	291.35	−0.29† ± 0.05	−0.17† ± 0.05	
				−0.31 ± 0.06	−0.17 ± 0.02	Cook[8]
	Robinson and Milstein[116]	1973			−0.20 ± 0.02	
	Simons and Salamon[117]	1974		−0.20 ± 0.02	−0.20 ± 0.02	
Tb	Jennings *et al.*[118a]	1957		−0.70 ± 0.08	0.55 ± 0.04	Cook[8]
$Fe_{96}Cr_{14}$	MacInnes and Schröder[96]	1970	1047.15 ± 0.14	−0.30 ± 0.04	0.0 ± 0.035	
$Fe_{90}Cr_{10}$	MacInnes and Schröder[96]	1970	1017.88 ± 0.14	−0.38 ± 0.04	0.205 ± 0.015	
$Pd_{0.9946}Mn_{0.0054}$	Boerstoel and Wielinga[124]	1970	1.98	−1.78	−0.14	
$Pd_{0.9865}Mn_{0.0135}$			4.477	−1.36 ± 0.12	−0.20 ± 0.06	
$Pd_{0.9755}Mn_{0.0245}$			5.783	−1.18	−0.41	
$K_2CuCl_4 \cdot 2H_2O$	Miedema *et al.*[126,127]	1963	0.883	0.0	0.0	
				−0.02 ± 0.13	0.03 ± 0.14	Cook[8]
				−0.041 ± 0.014	−0.041 ± 0.014	Lederman *et al.*[23]
$LiTbF_4$	Ahlers *et al.*[24]	1975	2.885	−0.148 ± 0.017	−0.148 ± 0.017	
Fe_3O_4	Grønvold and Sveen[130]	1974	848.7 ± 0.3	−0.35 ± 0.15	+0.05 ± 0.10	
EuO	Teaney[134]	1965		~0	~0.1	
				−0.50 ± 0.15	0.34 ± 0.24	Cook[8]
	Salamon[136]	1973	69.33	−0.026‡ ±0.005	−0.026‡ ±0.005	
				−0.09§ ±0.01	−0.09§ ±0.01	
	Kornblit *et al.*[181]	1973		−0.04 ± 0.03	−0.04 ± 0.03	
	Kornblit and Ahlers[137]	1975		−0.044 ± 0.01	−0.044 ± 0.01	
				−0.10¶ ± 0.05	−0.10¶ ± 0.05	
EuS	Van der Hoeven *et al.*[139]	1968	16.4265 ± 0.0005	−0.25 ± 0.03	0.00 ± 0.03	
					−1/16	Domb[268]
				−0.25 ± 0.03	0.00 ± 0.02	Cook[8]
$Mn(CH_3COO)_2 \cdot 4H_2O$	Schelleng *et al.*[158]	1968	3.18	0.14 ± 0.02	−0.19 ± 0.04	Cook[8]
$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Rayl *et al.*[159]	1968	0.176	0.125	0.125	
				−0.26 ± 0.06	0.10 ± 0.05	Cook[8]

†Results after correction for rounding are $\alpha' = -0.32$; $\alpha = -0.09$.
‡Inner region, $\epsilon < 10^{-2}$.
§Outer region, $\epsilon > 10^{-2}$.
¶After inclusion of singular correction terms.

reduced and moved towards lower temperature. This behavior has been discussed with reference to recent theories.[264,265] Values of α and T_c are to be reported in a later paper.

More recent measurements by AC-calorimetry[117] were tested for conformity to the scaling hypothesis and found to agree with $\alpha' = \alpha = -0.20 \pm 0.02$. The resistivity of gadolinium was found to agree better with $\alpha' = \alpha = 0.1$. No explanation could be given for the poor agreement with the Fisher–Langer[266] theory, which states that the magnetic contributions to the temperature derivative of the electrical resistivity and the heat capacity of a ferromagnet should correspond proportionately near the Curie-temperature. Better heat capacity measurements on high-purity material are needed for a further testing of conformity to the scaling hypothesis.

For two iron-chromium alloys, MacInnes and Schröder[96] found negative critical exponents below T_c. Considerably more negative values were found for three palladium-manganese alloys by Boerstoel and Wielinga[124] below T_c. Further measurements on alloys are needed to clarify the situation.

Heat-capacities on four copper(II) halide complexes have been determined by Miedema *et al.*[126,127] The behavior of $K_2CuCl_4 \cdot 2H_2O$ was analyzed in detail and found to correspond to a logarithmic divergence both below and

above T_c. According to Cook[8] the uncertainty in the exponent values is large, while Lederman *et al.*[23] insist on slightly negative exponents, characteristic of dipolar behavior.

Very recently the interesting dipolar Ising ferromagnet $LiTbF_4$ has been studied by Ahlers *et al.*[24] From theory[267] it is expected that a logarithmic term occurs for $d = 3$ in uniaxial magnetic systems with dipolar interactions. The heat capacity data were first analyzed in the ordinary way with the statistically allowed constraint $\alpha' = \alpha$, which resulted in $\alpha' = \alpha = -0.148 \pm 0.017$ and $A/A' = 0.242 \pm 0.007$. These results could not be understood in terms of known critical behavior involving short-range forces. The measurements were therefore analyzed for logarithmic contributions according to the prediction by Larkin and Khmelnitski[267] and the power of the leading term was found to be 0.34 ± 0.03 (prediction: 1/3).

Chalcogenides. For the chromium tellurides Cr_5Te_6, Cr_3Te_4 and Cr_2Te_3 the transition behavior due to the disappearance of the ferromagnetism has been studied.[128] The heat capacity maxima are rather broad, and in the case of Cr_3Te_4 not very distinct. The cause of the unusual behavior of Cr_3Te_4, as well as the effect of non-cooperative magnetic contributions to the heat capacity need to be investigated more closely before accurate critical exponents can be extracted.

The excess heat capacity due to the change from ferri- to paramagnetism in Fe_3O_4 has been evaluated and critical exponents determined.[130] The general conclusion of the extensive analysis was that below T_c the critical exponent remained negative under all conditions imposed, which is the situation most commonly encountered according to Cook.[8] Above T_c the assumptions made about the dilation contribution seriously influenced the α-value, and it could only be concluded that it was close to zero, corresponding approximately to logarithmic behavior in the magnetic heat capacity.

The most thoroughly studied chalcogenide compound is europium monoxide. According to Teaney[134] who used the standard calorimetric technique with step-wise energy inputs, the critical exponent is negative below T_c and approximately zero above T_c. His results were analyzed by Cook[8] in terms of a definitely negative critical exponent below and a slightly positive exponent above the critical temperature. AC-calorimetric measurements by Salamon[136] indicated a change in exponent value from -0.09 in the outer Heisenberg region to -0.026 in the inner ($\epsilon < 0.02$) dipolar region, in close accordance with theoretical prediction. In more recent calorimetric results by Kornblit and Ahlers[137] there was no evidence for changing exponents due to "cross-over" from short range to dipolar force behavior. In the range $0.005 \leq \epsilon \leq 0.07$ the values $\alpha' = \alpha = -0.044 \pm 0.01$, $A/A' = 1.22 \pm 0.06$ were chosen as the best estimates resulting from a pure power-law analysis. These results, although consistent with the scaling predictions, disagree with results of renormalization group calculations for isotropic ferromagnets with dipolar interactions. They were therefore reanalyzed after inclusion of a singular correction term, $D\epsilon^x$, with $x \approx 0.5$ according to theory. The critical exponents were then $\alpha' = \alpha = -0.10 \pm 0.05$, consistent with the theoretical predictions, but it should be noted that inclusion of the correction terms did not substantially improve the quality of the fit.

The heat capacity of the isostructural compound europium monosulfide was first studied by Moruzzi and Teaney,[138] and later more accurately in the critical region by van der Hoeven *et al.*[139] The results of the latter definitely indicated a negative α-value below T_c and logarithmic behavior above, and the same conclusion was reached by Cook.[8] Domb[268] compared the results by van der Hoeven *et al.*[139] above T_c with series expansion calculations, and found very satisfactory agreement for $\alpha = -1/16$. The importance of comparing critical exponents not only with theory but also with the actual transitional heat capacity, was stressed by Domb.

Accurate heat capacity determinations have been made on uranium monosulfide[140] and uranium monoselenide,[141] but critical exponents have not yet been evaluated from the data.

Pnictides. For this substance class no critical exponents have yet been derived. In some cases no primary data have been reported ($UN_{1.59}$ and $UP_{1.35}$ and lanthanoide compounds) and in other ($Mn_{2.00}Sb$, $Mn_{2.10}Sb$) heat capacities have not been measured at close enough intervals to permit precise evaluation of critical exponents.

The transition around 316 K in MnAs differs from most other ferro- to paramagnetic transitions in being discontinuous. The possibility of a magnetic transformation becoming first-order was considered by Bean and Rodbell,[269] who found that this could occur if the exchange energy were a sufficiently sensitive function of lattice volume or distortion, and that this was indeed the case for MnAs.

From the low-temperature side the transition starts out as a higher order magnetic one which then turns into a first order transformation close to 315K. The heat capacity did not become infinite, however, but remained very high over eight consecutive runs from 315.1 to 316.6K with accumulated equilibration periods of more than 2.5 days. It was confirmed by X-ray diffraction that the phase change from the NiAs- to the MnP-type structure occurred over a range in temperature, but the origin of this phenomenon has not been clarified. The assignment of a definite critical temperature to the transition in the sample studied was uncertain, and the evaluation of a critical exponent has therefore not been attempted.

b. *Antiferromagnetic substances*

Metals. Simultaneous measurements of the heat capacity and the resistivity of chromium near the Néel temperature were carried out by Salamon *et al.*[167] The large positive critical exponent value below the transition temperature, see Table 6, differs sharply from the prediction of the molecular field theory. This was not unexpected in view of the large energy gap and the small entropy of transition which indicates that only a small fraction of the electrons play a role in the magnetic transition. No critical exponents have yet been determined for the transition in manganese around 95K.

Samarium shows α-type maxima in its heat capacity near 13 and 105.8K. It was first studied by Roberts[172b] and later by Jennings *et al.*[172c] Critical exponents for the 105.8K transition were evaluated by Cook[8] with a negative exponent below T_c and a positive one above.

Halides. The heat capacity results for chromium(II) chloride by Stout and Chisholm[176] gave negative critical exponents both below and above T_c according to Cook.[8] The heat capacity singularity in manganese(II) fluoride was evaluated by Teaney[178] in terms of a logarithmic divergence below T_c and a possibly stronger divergence above T_c ($0 < \alpha \leq 0.1$). No critical exponents were determined for potassium manganese(II) trifluoride, but for the

Table 6. Critical exponent data for antiferromagnetic substances

Substance	Authors	Year	T_c/K	Crit. exp. α'	Crit. exp. α	Evaluator
Cr	Salamon *et al.*[167]	1969	311	0.34		
Sm	Jennings *et al.*[172c]	1959	105.8	-0.27 ± 0.10	0.60 ± 0.09	Cook[8]
$CrCl_2$	Stout and Chisholm[176]	1962	16.06	-0.75 ± 0.50	-0.50 ± 0.30	Cook[8]
MnF_2	Teaney[178]	1965	65.3	0.0	0.0–0.1	
$RbMnF_3$	Teaney *et al.*[180]	1966		~0.0	~0.0	
	Kornblit and Ahlers[22,181]	1973	83.08	-0.14 ± 0.01	-0.14 ± 0.01	
				-0.140 ± 0.004	-0.140 ± 0.004	Lederman *et al.*[23]
				-0.137 ± 0.004	-0.137 ± 0.004	Kornblit and Ahlers[137]
$MnCl_2 \cdot 4H_2O$	Friedberg and Wasscher[189]	1953		-0.27 ± 0.20	0.63 ± 0.10	Cook[8]
	Dixon and Rives[190]	1969		0.0	0.35 ± 0.02	
				0.19 ± 0.09	0.12 ± 0.11	
FeF_2	Ahlers *et al.*[196]	1974	78.26	0.157 ± 0.016	0.157 ± 0.016	
				0.112 ± 0.044	0.112 ± 0.044	
$CoCl_2$	Chisholm and Stout[184]	1962	24.71	-0.39 ± 0.05	0.57 ± 0.06	Cook[8]
$CoCl_2 \cdot 6H_2O$	Skalyo and Friedberg[203]	1964	2.2890	0.0	0.0	
Rb_3CoCl_5	Blöte and Huiskamp[205]	1969	1.14	1/8	1/8	
Cs_3CoCl_5	Wielinga *et al.*[206]	1967	0.523	0.0	0.75 ± 0.05	
				0.19 ± 0.04	0.50 ± 0.05	Cook[8]
$CoBr_2 \cdot 6H_2O$	Kopinga *et al.*[208]	1974	3.150	0.0	0.0	
Cs_3CoBr_5	Wielinga *et al.*[206]	1967	0.282	0.0	0.0	
$CuCl_2$	Stout and Chisholm[176]	1962	23.91	-0.70 ± 0.26	0.05 ± 0.20	Cook[8]
$GdCl_3 \cdot 6H_2O$	Huiskamp[164]	1966	0.185		0.33	
$ErCl_3 \cdot 6H_2O$	Lagendijk *et al.*[217]	1970		-0.26 ± 0.06	-0.07 ± 0.05	
UI_3	Roberts and Murray[218]	1955		0.8 ± 1.0	-0.4 ± 1.0	Cook[8]
Fe_2O_3	Grønvold and Samuelsen[233]	1975	955.0	-0.50 ± 0.10	0.15 ± 0.10	
Er_2O_3	Culbert *et al.*[243]	1974	3.3707	0.125	0.125	
$GdVO_4$	Cashion *et al.*[257]	1970	2.50		0.30	
$DyPO_4$	Colwell *et al.*[258]	1969	3.39		0.35	
$Dy_3Al_5O_{12}$	Keen *et al.*[259]	1967	2.49		0.31	
	Wolf *et al.*[261]	1972	2.49 ± 0.01	~0	0.2 ± 0.1	
Yb_2O_2S	Rossat-Mignod *et al.*[262]	1972	2.575	0	0.4 ± 0.05	

related rubidium compound Teaney *et al.*[180] also concluded that $\alpha = 0$, or was possibly slightly positive ($0 < \alpha < 0.05$). New series of measurements on two very homogeneous samples of $RbMnF_3$ were carried out by Kornblit and Ahlers.[22,181] The exponents derived from the ordinary calorimetric heat capacity measurements below and above T_c were equal. The common value was negative ($\alpha' = \alpha = -0.14 \pm 0.01$), which implies that the heat capacity is finite at T_c. Reanalyses by Lederman *et al.*[23] and Kornblit and Ahlers[137] gave the same result. The exponent value for this isotropic antiferromagnet ($d = 3$, $n = 3$) with negligible dipolar forces is in good agreement with the calculations, (Table 1), when the singular correction term, $D\epsilon^x$, and the term $E\epsilon$ to account for changing lattice heat capacity in the critical region were included in the analysis.

No analysis of the existing measurements on anhydrous manganese(II) chloride has apparently been carried out. For the manganese(II) chloride tetrahydrate the measurements by Friedberg and Wasscher[189] were analyzed by Cook[8] in terms of a negative exponent below and a positive one above T_c, see Table 6. Later, Dixon and Rives[190] interpreted their measurements in terms of a logarithmic behavior below T_c and a slight divergence above.

Iron(II) fluoride is considered to be a uniaxial antiferromagnet because of its large anisotropy. The transition behavior is thus expected to conform to the liquid–gas case with $\alpha' = \alpha = 1/8$. The available experimental results[195,196] gave accordingly $\alpha' = \alpha = 0.157 \pm 0.016$ without the singular term $D\epsilon^x$ and the lattice term $E\epsilon$ included in the analysis, and $\alpha' = \alpha = 0.112 \pm 0.044$ when these terms were included. Thus, the results support the theoretically predicted universality of critical point parameters.

The heat capacity data for cobalt(II) chloride by Chisholm and Stout[184] were evaluated by Cook[8] in terms of a negative exponent below T_c and a positive one above. Similar results were obtained by Cook[8] for the cobalt(II) chloride hexahydrate studied by Skalyo and Friedberg,[203] in contrast to their own estimate of logarithmic critical behavior both below and above T_c.

For three of the four remaining cobalt halide compounds listed in Table 6 logarithmic heat capacity behavior seems to obtain in the critical region. For the fourth, trirubidium cobalt(II) pentachloride, Wielinga *et al.*[206] reported a strong divergence above T_c, and this was to some extent substantiated by Cook.[8]

The heat capacity results on copper(II) chloride by Stout and Chisholm[176] gave a substantial negative value of $\alpha' = -0.70 \pm 0.26$ below T_c according to Cook,[8] while α was close to zero. Again, the difficulty in getting a good approximation of the lattice heat capacity might be the cause of the unusually low α' value.

From the heat capacity determinations on gadolinium(III) chloride hexahydrate by Wielinga it was concluded by Huiskamp[164] that a rather strong divergence is present above T_c, while for the related erbium(III) compound Lagendijk *et al.*[217] found negative exponents both below and above T_c. For the measurements on uranium(III) iodide by Roberts and Murray,[218] Cook[8] reports a considerable positive exponent value below T_c and a negative one above, but these unusual values are extremely uncertain and need further verification.

Chalcogenides and pnictides. For these types of antiferromagnetic compounds critical exponent data are virtually non-existent.

For float-zone refined single crystals of erbium(III)

oxide, Culbert *et al.*[243] obtained heat capacity data to $\epsilon \approx 10^{-4}$ with no rounding-off effect. The results were found to conform with the expected exponent values for the three-dimensional Ising model ($\alpha' = \alpha = 0.125$). The actual heat capacity values were, however, only half of the theoretical ones[30,32] and this was ascribed to incomplete ordering of the system.

The transitional heat capacity is often found to differ considerably even for related substances. Thus, manganese disulfide, which was studied in the form of large natural single crystals, showed a rather sharp heat capacity maximum, (Fig. 4), while manganese ditelluride showed a rounded, broad one. The cooperative heat capacity and transitional entropy are only a fraction of that expected for randomization of spin 5/2. Although it is tempting to ascribe the sharp heat capacity peak for MnS_2 to crystal perfection, another possible cause of the difference between the two compounds lies in the coupling of the cooperative magnetic mode with other modes of transition.

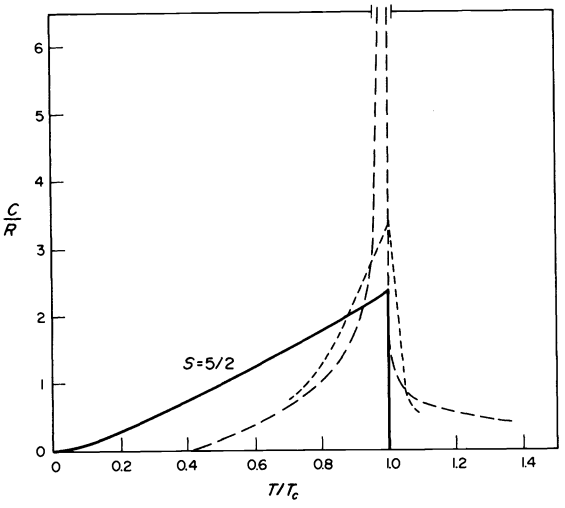

Fig. 4. Cooperative magnetic heat capacity of manganese disulfide[226] ---, and manganese ditelluride[226] --- on a reduced temperature scale. The molecular field theory behavior for $S = \frac{5}{2}$ is shown for comparison.

Antiferromagnetic chromium monoantimonide with the hexagonal NiAs-type structure has been studied by the author in the critical region. Even though the sample was in form of a polycrystalline powder, the heat capacity at 685 K rises to rather high values. This can be seen from Fig. 5 where the theoretical results for the three-dimensional Heisenberg model with infinite spin has been drawn for comparison, and also the results for iron(II) fluoride,[194] which are among the highest measured on a molar basis. The steepness of the maximum is also reflected in the derived critical exponents: $\alpha' \approx \alpha \approx 0.50$. The cause of these high values is not yet clear.

Finally, the highly interesting work on dysprosium aluminum garnet ($Dy_3Al_5O_{12}$) in magnetic fields[259-261] should be mentioned. With increasing magnetic field the heat capacity peak of the antiferro- to paramagnetic transition is reduced and shifted to lower temperature. A magnetic field of 7.5 kOe completely suppresses the transition, while at an intermediate field a tricritical point is present and the transition becomes first-order. In the

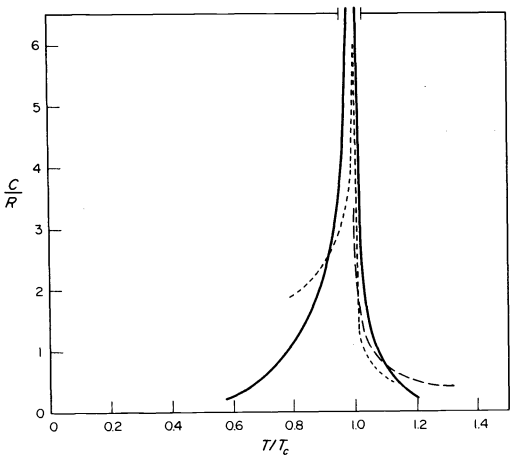

Fig. 5. Cooperative magnetic heat capacity for chromium monoantimonide ——. Values for iron(II)fluoride[194] · · · ·, and for the three-dimensional Heisenberg model with infinite spin --- are also shown.

preliminary critical analysis an excellent fit was found with $\alpha = 0$. The authors stress that this must be regarded as an empirical statement only, and not related to theoretical predictions of the asymptotic form due to significant smoothing of the experimental data. The choice of T_c was shown to seriously influence the resulting α'-value, and the theoretical values 1/8 would arise by choosing $T_c - T_{max} = 1.05$ mK, in close agreement with the analysis by Gaunt and Domb.[32] Above T_c the analysis is easier since the asymptotic form should be valid over a considerably wider range (to $\epsilon = 10^{-2}$), and the value $\alpha = 0.2 \pm 0.1$ was derived.

4. *Structural order-disorder transitions*

A classical example is β-brass which is an approximately equiatomic mixture of copper and zinc. It was studied by Sykes and Wilkinson[270] and by Moser[271] by continuous adiabatic shield calorimetry. Just as for magnetic transitions, the heat capacity was found to rise continuously as the transition temperature ($T_c = 739$K) was approached from the low temperature side, and decrease rather sharply above the critical temperature. Moser's results were believed for a long time to support the older theories which predicted a functional discontinuity. Recent X-ray and neutron diffraction investigations[272] of the transition have indicated good agreement between other experimentally determined critical exponents β, γ and ν and those calculated for the three-dimensional Ising model. Thus, the heat capacity behavior should presumably also be Ising-like. In the actual determination by AC-calorimetry Ashman and Handler[273] found good agreement with the Ising model calculations above T_c both for the exponent ($\alpha = 0.13 \pm 0.01$) and the magnitude of the transitional heat capacity, while below T_c the heat capacity depended roughly logarithmically on ϵ in the range $10^{-5} < \epsilon < 10^{-2}$ ($\alpha' = -0.01 \pm 0.01$). The relative C_p data obtained from the ΔT vs T curves were normalized at 810°K to Moser's determinations. The values of C_V used in the analysis were derived from C_p by applying the Pippard relations between heat capacity, thermal expansivity and isothermal compressibility.

This violation of the universality hypothesis and the

different amplitude ratio A'/A from that observed for many liquid–gas transitions led Salamon and Lederman[274] to re-analyze the experimental results on β-brass obtained by Ashman and Handler.[273] The assumption that C_V should follow the ideal heat capacity of an Ising system rather than C_p was questioned by Salamon and Lederman as it had been shown by Baker and Essam[275] that the thermal expansivity near the critical point more strongly renormalizes the exchange interaction at constant volume than at constant pressure. In the reanalysis Salamon and Lederman used the functional form

$$C = \frac{A}{\alpha}(\epsilon^{-\alpha} - 1) + B + C\epsilon$$

where the linear term in ϵ was included to account for less singular parts of the transitional heat capacity, and the temperature variation in the lattice heat capacity. They then tested the scaling hypothesis $\alpha' = \alpha$ by choosing a common T_c and C value to give the maximum linear correlation coefficient. Having established a linear relationship between the transitional heat capacity above and below T_c the data sets were merged into a single function of ϵ to determine the common critical exponent. The value $\alpha = 0.11 \pm 0.02$ and the derived amplitude ratio A^+/A were consistent with those for other Ising-like materials and provide further experimental verification of the universality hypothesis.

In the case of interstitial solid solutions like β-brass the singular behavior is expected to be most pronounced at the stoichiometric 1:1 atomic ratio—which has not been studied, as it falls outside the homogeneity range of the β-brass phase. In subtractive solid solutions on the other hand, the structural order is complete at the limiting stoichiometric composition at low temperature, while slightly non-stoichiometric samples remain partly disordered. With increasing concentration of vacancies, the atoms on partly occupied lattice sites might order completely at certain compositions—and thus also the vacancies.

An example of this is found in the nickel–selenium system for which Sheveleva, Gerassimov, Lazarev and Geiderich have presented new data at this meeting. We have made high temperature heat capacity measurements on a dozen samples within the homogeneity range of the $Ni_{1-x}Se$ phase with NiAs-like structure.[276,277] Our results over the transition region for those with about 14, 15 and 16% vacancies on the nickel lattice are shown in Fig. 6. It is remarkable that the heat capacity maximum, and highest transition temperature are not obtained for a sample with a simple stoichiometric ratio like 7:8 but instead only at one higher number ratio, possibly 54:64 or 61:72.

5. *Binary liquid and solid mixtures at the critical solution temperature*

Heat capacity data on binary liquid mixtures have shown striking divergencies near the consolute points. Thus, the observed increases in C_p in binary fluids vary from about 20 J K^{-1} mol^{-1} in the CH_3OH–C_6H_{12} system[278] to about 160 J K^{-1} mol^{-1} in the CCl_4–$C_6F_{11}CF_3$ system.[279]

Large increases in heat capacity were also observed at different compositions in the binary liquid systems Ne–H_2,[280] Ne–D_2[281] and H_2O–$(C_2H_5)_3N$,[282] indicating that composition is not particularly important for the phenomenon.

The results by Shripov and Kostin on the triethylamine–water[282] and triethylamine–heavy water[283] systems were analyzed by Blazoi and Gusak,[284] who found $\alpha' = \alpha = 0.2$ for both systems. Brouwer *et al.*[280] measured the heat capacity of liquid mixtures of neon and hydrogen over the whole phase separation range. They analyzed the results for a sample with critical composition and got $0 < \alpha' < 0.2$.

The saturated heat capacity of the binary liquid mixture tetrafluoromethane–trifluoromethane was measured near the upper consolute point at 132K by Cope, Reamer and Pings.[285] Results below and above the critical temperature showed a λ-like behavior which was compatible with $0 \leq \alpha' = \alpha \leq 0.1$.

Probably the first measurements on the heat capacity in the consolute region of a liquid alloy were carried out by Schürman and Parks[286] for 49.74% mercury in gallium amalgam. It was measured by a heat pulse technique with

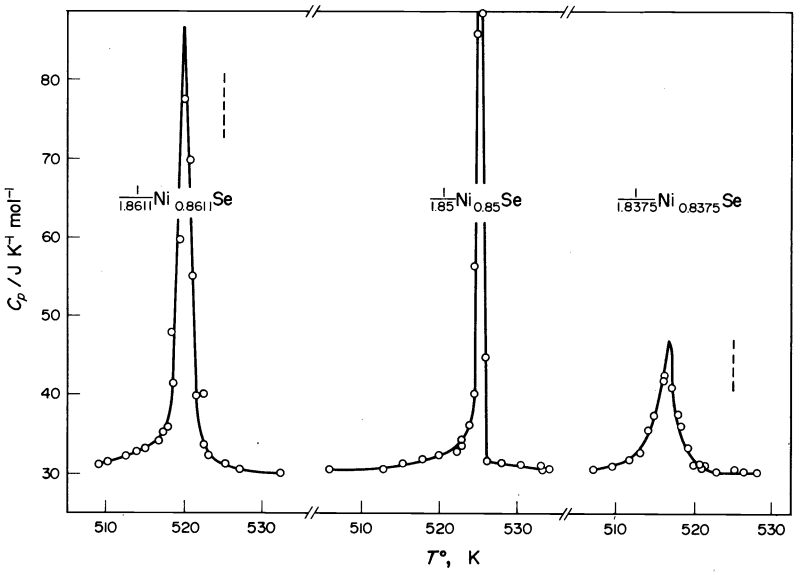

Fig. 6. Heat capacities for $Ni_{0.8611}Se$, $Ni_{0.85}Se$, and $Ni_{0.8375}Se$ in the structural order-disorder transition region.

isothermal shield down to $\epsilon \simeq 10^{-5}$ above T_c. A critical exponent $\alpha = 0.3 \pm 0.1$ was deduced. Thus the binary metallic mixture did not show markedly different behavior from the non-conducting binaries, and the earlier contention of Egelstaff and Ring[287] that the interatomic forces affect the critical exponent values was not substantiated.

It seemed of interest to Greer, Levelt Sengers and Furukawa[288] to investigate whether such an anomalous heat capacity could also be found in a binary solid system and they studied argon–methane. The homogeneous solid solution consisted of argon and methane molecules on the same lattice. In this case the measurements by adiabatic pulse calorimetry had to be confined to the one-phase region because true equilibrium could not be obtained once the system had separated into two phases.

Greer *et al.* did not observe any large increase in the heat capacity at the solid–solid consolute point (62K, 65% Ar). They assumed that if the range of interactions of the strains, due to the size difference, was approximately equal to the correlation length, the critical fluctuations would be damped and the heat capacity would follow the molecular field theory rather than the Ising model theory.

6. *Ferro- and antiferroelectrics*

Ginzburg[289] estimated the coherence length in barium titanate ($BaTiO_3$) and concluded that the Landau theory should be valid when $\epsilon > 10^{-4}$ in the ferroelectric case. λ-shaped peaks occur in the heat capacity of many compounds, but most of the reported results do not even allow a qualitative conclusion about the details of the singularity. For extensive references and illustrations of heat capacity and other property behavior of ferro- and antiferroelectrics, see Landolt-Börnstein.[290]

Heat capacity measurements have recently been carried out by Deutsch and Litov[291] on caesium dihydrogenarsenate near the ferroelectric phase transition at 146.23K. Just as with all other KH_2PO_4-type crystals studied so far, CsH_2AsO_4 also undergoes a first-order transition, but two thirds of the total transitional entropy, which is 4.2 J K^{-1} mol^{-1}, was acquired before the structural change and loss of spontaneous polarization took place. It should also be noted that the heat capacity tail above T_c is very small, which is in contrast to what has been observed for KD_2PO_4 and KH_2AsO_4. No critical exponents were derived.

For tin(II)chloride dihydrate and dideuterate the heat capacity behavior in the transition range, attributed to an order-disorder change in the hydrogen (or deuterium) bonded network, was studied by Matsuo *et al.*[292–294] The derived critical exponents for $SnCl_2 \cdot 2H_2O$ were consistent with the scaling prediction $\alpha' = \alpha$, but the value $\alpha = 0.49 \pm 0.02$ is notably large. A first-order component amounting to 34 J mol^{-1} was observed at the heat temperature 217.994 ± 0.01K. Even though it only corresponds to 3.3% of the total transitional entropy of 4.6 J K^{-1}, it might seriously influence the critical behavior.

The heat capacity of squaric acid (3,4-dihydroxocyclobutene-1,2-dione) in the possible antiferroelectric transition region around 373K is currently being studied.[295] The polycrystalline sample was provided by Semmingsen who has determined the crystal structure of the compound.[296] The structure was found to change from monoclinic to tetragonal at about 370K and partial birefringence studies indicated a very wide critical region.[297] The heat capacity results (Fig. 7), also indicate that the critical region below T_c is wide, and thus confirm that the interactions responsible for the transition must be short range. This is generally the case for antiferroelectric transitions, since the range of zero temperature correlations are shorter than for the ferroelectric ones. Thus, no similar preservation of the molecular field theory is expected, and this makes the antiferroelectric substances especially interesting study objects. Critical exponents for squaric acid are now being evaluated.

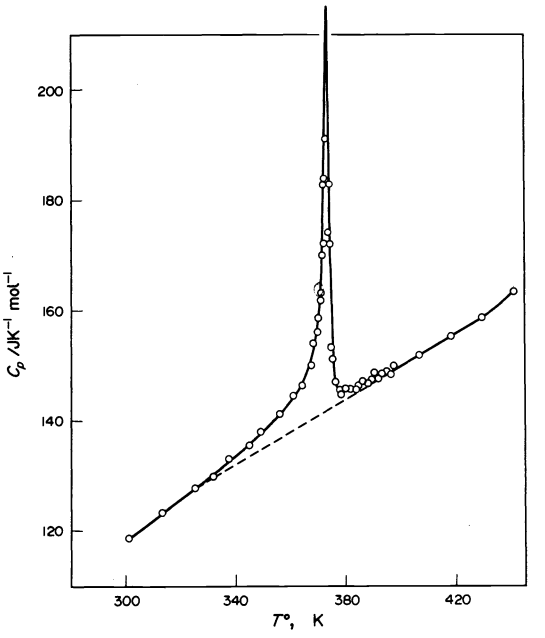

Fig. 7. Heat capacity of squaric acid.

7. *Superconductors*

For pure superconductors the large coherence length indicates[4] that deviations from the Ginzburg–Landau theory should not occur before ϵ gets as small as 10^{-14}.

In the course of the last two decades the heat capacity of nearly all elemental semiconductors has been studied and compared with the Bardeen–Cooper–Schrieffer theory of superconductivity.[298] One of the last to be studied was osmium.[299] The rise in heat capacity in the superconducting region is in good agreement with theory, with seemingly only a slight further excess heat capacity as the transition temperature is approached from below. The drop in heat capacity from superconducting to normal state occurs within 1 mK. Thus there seems to be little hope of demonstrating critical heat capacity behavior for pure superconductors with present techniques, but as reported by Dr. Philips at this meeting, there are other interesting phenomena connected with alloying and impurities in superconductors that merit study.

8. *Fusion*

Finally let me shortly touch upon the fusion process. Here the first-order component is immensely large and the influence of impurities of such paramount importance that any critical behavior, in a sense similar to what we have been discussing so far, has not yet been definitely established in pure elementary substances.

In a study of the fusion of nominally 99.9999 mass % pure bismuth[300] a premonitory phenomenon was observed. Its magnitude corresponded, however, to that for the presence of about 10 atoms per million of solid-insoluble/liquid-soluble impurities. If the pre- and post-melting heat capacity are plotted on a log–log scale,

(Fig. 8), the straight line below the maximum indicates a critical exponent $\alpha' = 1.9$. This is close to the value 2 expected for a liquid-soluble/solid-insoluble impurity which could well have been present in the necessary amount. It thus remains to be demonstrated on even purer samples what is really the effect of the rapid multiplication of dislocations or other defects in the region just below fusion.

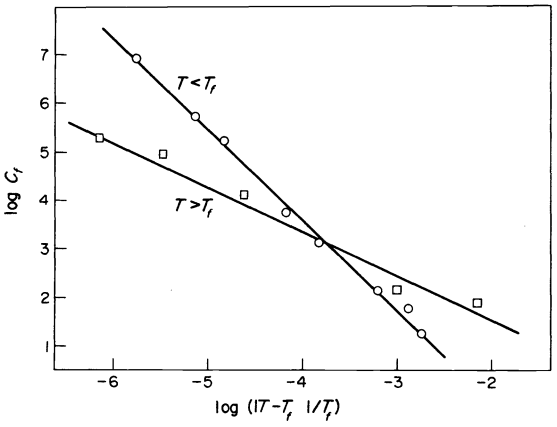

Fig. 8. Pre- and postmelting heat capacity of bismuth vs $|T - T_f|/T_f$ on a log–log scale.

Above the maximum the critical exponent was found to be $\alpha = 0.6$. The phase behavior above the liquidus line is, however, principally different from that in the solidus–liquidus region, and an exponent value closer to that observed for other critical phenomena is pleasing. The value, although higher than expected for ordinary critical phenomena, is rather close to that observed for the transition in $SnCl_2 \cdot 2H_2O$ where a first-order component is also present.[293]

In concluding I hope that some of the phenomena and problems I have discussed will merit further investigation heat capacity-wise, in some cases also under varying pressure and or magnetic field etc. Furthermore, the evaluation of critical exponents should be considered as a fertile territory not only for solid state physicists, but also by thermodynamicists in order to characterize and systematize the transitions which we are studying.

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