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QUANTITATIVE CHARACTERISTICS OF THE SPECIFIC HEAT SINGULARITY IN SECOND-ORDER PHASE-TRANSITION POINTS

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A study was made of the influence of different imperfections of the samples and subjective errors occurring in the reduction of the experimental results on the character of the singularity of the specific heat near second-order phase transition points in solids. An analysis of the experimental data gives grounds for hoping to classify second-order phase transitions and to estimate their closeness to the Ising model by using the results of specific-heat measurements.

INTRODUCTION

A rather large number of recent papers are devoted to the measurements of the specific heat near the second-order phase transition points in solids.[1-6] All these investigations revealed an approximately logarithmic singularity of the specific heat on approaching the transition points both from the right ($T > T_c$) and from the left ($T < T_c$):

$$C_+ = -A_+ \ln t + B_+, \quad C_- = -A_- \ln t + B_-, \quad t = |T - T_c| / T_c. \tag{1}$$

The concrete characteristics of these singularities, however, show surprising discrepancies. Some of the authors[1-6] state that the singularity is symmetrical with respect to T_c(($A_+ = A_-$), so that the concept of the jump on the specific heat

$$\Delta C = \lim_{t \to 0} |C(-t) - C(t)| = B_- - B_+ \tag{2}$$

remains in force. In [2,4,5] it is stated that the coefficients of the logarithmic function are not equal ($A_+ < A_-$). Thus, $\Delta C \to \infty$ and the concept of the specific-heat jump becomes meaningless. Certain authors[7] propose that the specific heat is not expressed by the logarithmic function (1) at all on the side of the disordered phase, and should be approximated (incidentally, quite closely) by a power law expression (3) with a small exponent:

$$C_+ = A_+ t^{-\alpha} + B_+. \tag{3}$$

This exponent α is assigned values from 0.05 to 0.2 in various papers.

The experience obtained in this region causes us to doubt all the categorical statements on this subject. We propose that the greater part of the differences in the singularities is due to imperfection of the samples and the ensuing incorrect determination of T_c, which in this case becomes an additional arbitrary parameter. Therefore, before we draw any conclusions concerning the details of the singularities, we must study the influence of different imperfections on the observable C(T) dependences, and only then can we attempt to deduce the limiting characteristics (for ideal samples). In the present paper we continue the study of this influence on solids and show by means of experiments that it is premature to draw any conclusions concerning the correctness of (1) or (3) at the present status of the samples.

We measured the specific heat of gadolinium, magnetite (Fe_3O_4), and vanadium deuteride ($VD_{0.8}$) in the vicinity of the phase transition. The adiabatic calorimeter with which the measurements were made has been described in the literature with sufficient detail.[8-10] The accuracy of the measurements of the specific heat was different in different experiments, and fluctuated between 0.2 and 1.5%, depending on the conditions. The perfection of the gadolinium sample, in view of its metallic nature, can be very approximately characterized by the ratio of the electric resistivities at room and helium temperatures $\rho(300^\circ K)/\rho(4.2^\circ K) = k$ (we shall accordingly label samples Gd_k). For the other samples

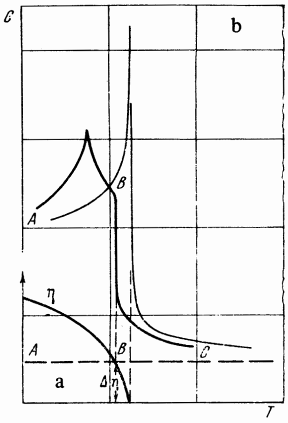

FIG. 1. Dependence of the ordering parameter η on the temperature near the second-order phase transition of an ideal sample (a) and dependence of the specific heat on the temperature of the same sample (b), measured at $\eta = 0$ (thin line) and at $\eta = \Delta\eta$ (heavy line, path ABC).

we do not have even this possibility. Therefore the results of the investigations are qualitative.

1. OBJECTIVE FACTORS INFLUENCING THE FORM OF THE SINGULARITY OF THE SPECIFIC HEAT

The singularity of the specific heat near the critical liquid-vapor point of several substances was investigated in earlier studies.[11-13] Assurance of the existence of a definite character of the singularity of this point, and the relatively large sensitivity of the substance in the critical state, which makes it possible to vary the main characteristic of the sample without greatly changing the experimental conditions, has made it possible to use the critical point as a model for the study[14-16] of the influence of different factors on the form of the singularity at the phase-transition points. The results of these investigations enable us to interpret correctly the data on the specific heat of solid samples in which the character of the imperfections is known very approximately.

We list here those factors which are significant for real samples, and which distort the true form of the dependences near the singular points, using the language of the existing theory of second-order phase transitions.[17]

1. A nonzero value of the ordering parameter at the transition point (the deviation of the average gas density from critical, the deviation of the composition of the binary alloy from stoichiometric, a nonzero average magnetic or electric moment of a ferromagnet or a ferroelectric, etc.). This factor was investigated in argon.[14] It was shown that it leads to a shift of the observed transition point towards the phase with the larger specific heat, to a difference between the temperatures of the maximum of the specific heat and of the jump, and to a lowering of the height and sharpness of the maximum and to a decrease of the magnitude of the jump. In Fig. 1 this case corresponds in schematized form to the path ABC. Such a deviation from ideal conditions, which is the same at all points of the sample, is due to the stray magnetic and electric fields, to the presence of surface charges in the ferroelectric,[18] to quenching, and to other volume defects of the sample.

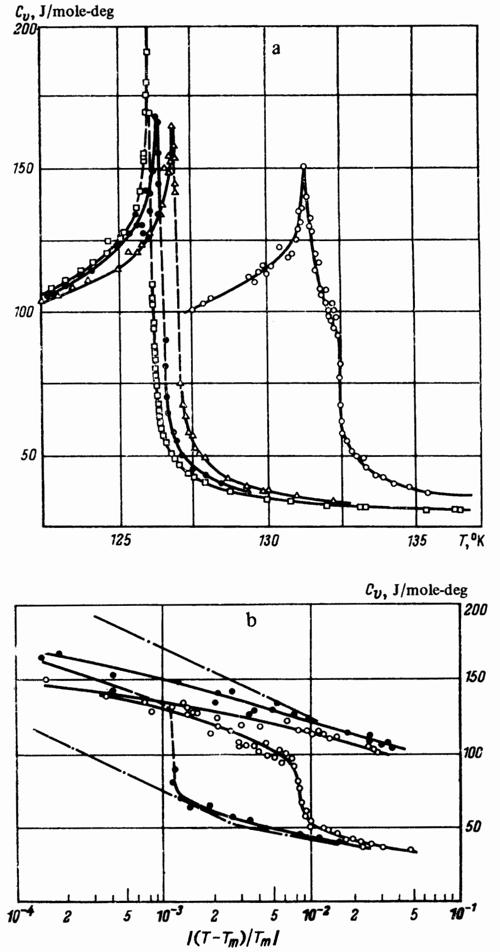

FIG. 2. Dependence of the specific heat on the temperature (a) for relatively pure nitrogen and for nitrogen contaminated with impurities: □ – N – 99.88%, O, Ar – ~0.12%; ● – N – 98%, O, Ar – 1 – 2%; Δ – N – 96.5%, O – 3.5%; ○ – N – 77,4%, O, Ar – 22.6% and the same data (b) shown on a semilogarithmic scale (T_m – temperature of maximum specific heat.

2. The presence of chemical impurities, point defects, possible impurities of another isotope, and similar factors, leading to a decrease of the effective dimension of the sample. All these lead also to a temperature difference between the jump and the maximum of the specific heat and to a lowering of this maximum. The influence of the impurities was investigated[15] at the critical point of nitrogen (Fig. 2a). The difference between the maximum and the jump of the specific heat, and the lowering and the shift of the temperature of the maximum, are clearly seen. The results are compared with the corresponding results of an investigation[9] of the Curie point of gadolinium, the degree of purity of which was estimated from the residual resistance. A qualitative agreement was observed (compare Fig. 2b and Fig. 5a below).

It should be noted that in this case the maximum of the specific heat must of necessity be shifted towards the ordered phase. This depends on the character of the added impurity: addition of oxygen, which has a higher critical temperature, to nitrogen raises the T_c of the mixture, while addition of nitrogen to argon, to the contrary, lowers the T_c of the latter. In ferromagnets, this corresponds to addition of magnetic and nonmagnetic impurities.

Figure 2 reveals also a new circumstance, namely that the jump is not perpendicular, as in Fig. 1b, but is

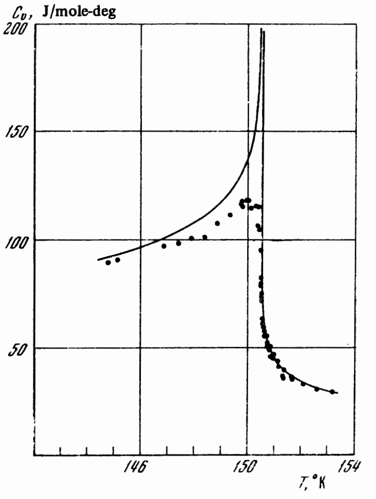

FIG. 3. Temperature dependence of specific heat of argon: solid curve – for homogeneous sample (with stirring during the measurement time) and ● for inhomogeneous samples (with hydrostatic distribution of the density) in the vicinity of the critical points.

spread out in temperature and represents, strictly speaking, not a jump but a more or less smooth bend of the curve. This circumstance is attributed to the inhomogeneity of the distribution of the impurity and reduces in final analysis to the factor discussed in the next section.

3. The inhomogeneous distribution of the factors of Secs. 1 and 2, due to the inhomogeneity of the physical state of the system. This is the smearing factor which is the most frequently encountered and most harmful to the singularity. In this case the maximum has a smooth top, and the jump stretches out in temperature, becoming transformed into a smooth bend. The influence of such an inhomogeneity was investigated at the critical point of argon.[16] The inhomogeneity of the state was specified in terms of the hydrostatic effect (i.e., the influence of the pressure of the upper layers of the liquid on the lower ones), which led to the following dependence of the density of the liquid on the height at the critical point:[19]

$$V - V_c \sim (h - h_0)^{1/3}. \tag{4}$$

Figure 3 shows the results of measurements of the specific heat of argon in the presence and absence of inhomogeneities.[16]

The experimentally measured specific heat is expressed in this case by the integral of the specific heat as a function of the density over the height of the vessel. On the other hand, the density is determined by expression (4). Since the singularity of the specific heat at the critical point is relatively weak (logarithmic), integration yields not an infinite peak but a finite rounded-off maximum, while the perpendicular jump leads to a smooth bending of the curve, depending on the character of the integrand distribution (4).

In solids one usually observes an inhomogeneity connected with uneven deformation of the crystallites in the polycrystal, distortion on the boundaries of the crystallites, differences in the composition along the sample, different degrees of quenching of different parts of the sample, differences in the contents of the impurities in the values of the crystals and near the surfaces, etc. The distribution of the defects and of the deviations from long-range order over the dimensions is probably Gaussian in such samples, and consequently differs greatly from (4). However, the experimentally measured specific heat is obtained by integrating this distribution over the entire sample, and it can be assumed that the detailed character of the integrand is immaterial in a qualitative approximation. Figure 4 apparently illustrates this premise.

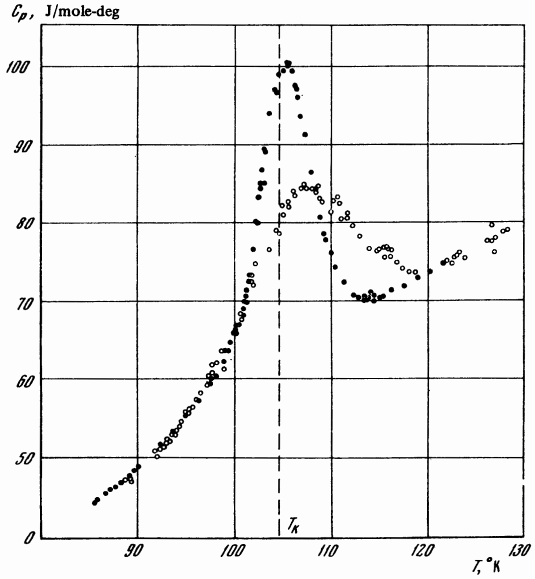

FIG. 4. Temperature dependence of specific heat of Fe_3O_4 near the low-temperature transition for single-crystal (●) and polycrystalline (○) samples.

The specific heat C_p of magnetite in the region of the phase transition, 110°K, was measured by us for two samples of approximately identical purity but different origin and structure. The black points in Fig. 4 correspond to the specific heat of natural single-crystal magnetite of irregular shape with transverse dimensions 1–2 cm, and the light points pertain to polycrystalline and powdered synthetic samples with grain dimensions 10^{-2}–10^{-3} cm. An x-ray analysis of the samples shows that in the polycrystalline sample the inhomogeneities of the structure are very strong, whereas the single crystal can be regarded as relatively homogeneous.[1)] The qualitative analogy between Figs. 3 and 4 is evident. The inhomogeneity of the state of the individual single crystals in the powder in conjunction with the large number of defects of the structure has led, just as in [16], to an almost complete smoothing of the peak of the specific heat of the powder, whereas for the single crystal it is quite clearly pronounced.

It seems to us that the foregoing three items complete the objective causes of the smearing of the singularities and serve as a basis for an approach to a correct organization of experiments on the study of the singularity of the specific heat near phase-transition points in solids.

2. SUBJECTIVE FACTORS LEADING TO A DISTORTION OF SINGULARITIES OF THE SPECIFIC HEAT

When working with imperfect samples (these can be meaningfully defined as those in which the smearing of

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[1)] The x-ray analysis of our samples was performed by B. Ya. Sukharevskiĭ and A. V. Alapina, to whom the authors are most grateful.

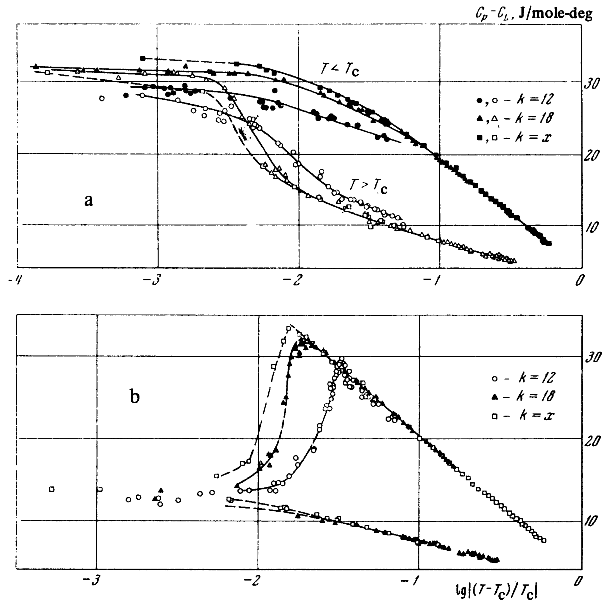

FIG. 5. Dependence of the "magnetic specific heat" $C_p - C_L$ (C_L – lattice specific heat) of Gd_k on log $|(T - T_c)/T_c|$ in the case when a) T_c is the temperature of the maximum of the specific heat and b) T_c is assumed to be the probable temperature of the vanishing of the magnetic order in the ideal sample, $T_c = 250°$ K: Gd_x–sample from [20], where probably $x \sim 30$; ● – Gd_{12}; ▲ – Gd_{18} □ – Gd_x.

the singularities exceeds the errors of our measurements) we are faced with the necessity of reconstructing the form of the investigated function (such as (1) or (3)) for an ideal sample from incomplete and distorted data. Since the exact characteristics of the imperfection in the sample are not available, we usually reduce the experimental data as in the case of ideal samples, and exclude the smearing region from consideration. The results obtained in this case seem convincing to many, and since various workers reduce their data differently, a seeming discrepancy between the results arises frequently. The sources of the errors are in this case the determination of the true temperature of the transition (the transition temperature for the ideal sample) and separation of the regular part of the function.

1. Since the phase transition in its exact meaning occurs in an infinite (see Sec. 2 of Part 1) homogeneous (Sec. 3 of Part 1) sample was a zero mean value of the ordering parameter (Sec. 1 of Part 1) it follows that, strictly speaking, there is no phase transition in the absence of imperfections in the sample. In a temperature region which is close to the transition temperature T_c of an ideal sample, however, the different properties of the real sample have considerable anomalies. It is clear for example from Fig. 1 that the maximum of specific heat of a sample with nonzero value of η is reached at a temperature much lower than T_c. The position of the jump of the specific heat is much closer to T_c. All the elements of the singularities shift even more under the influence of impurities—Fig. 2. Finally, it is also clearly seen in Fig. 3 that an inhomogeneous sample has a maximum of the specific heat far from T_c.

Thus, even if we assume that the form itself of the singularity remains unchanged (which is hardly possible), we must ascertain first the temperature to which this singularity pertains. The functions (1) and (3) are so sensitive to the value of T_c, that for most solid samples it is possible to satisfy any of these expressions by choosing T_c (in the case of function (3), the regular part is also significant (see Sec. 2 of Part 2)). Figure 5 shows our data on the specific heat of gadolinium samples Gd_k, the perfection of which is characterized by the quantity $k = \rho(300° K)/\rho(3.2° K)$, which depends on the residual resistance of the sample. On Fig. 5a, the values of T_c were chosen to fit the maximum of the specific heat, and consequently are different for different samples, while in Fig. 5b they were chosen to equal the temperature of the total vanishing of the magnetic order (including the so-called "magnetization tails"), which is probably the same for all the samples. It is clearly seen that in such imperfect samples the choice of T_c determines the point of view of the authors: Fig. 5a offers evidence in favor of Eq. (1) with $A_+ = A_-$, while Fig. 5b favors $A_+ \neq A_-$. The ratio of the slopes of the curves in Fig. 5b is in this case $A_-/A_+ = 3$, corresponding to the theoretical value expected from the assumption that computer calculations in accordance with the Ising model apply to real systems.[7] One must not overestimate, however, the importance of such an agreement: by varying T_c, it is possible to obtain also other values of A_-/A_+ in a narrow interval. It is necessary first to develop for the determination of T_c methods that are independent of the measured property, and only then can we study the limiting dependences of these properties themselves. To this end it is necessary to consider different properties of substances, to separate those that are least sensitive to the distorting factors, and to determine the values of T_c just from the latter. Generally speaking, there is no need for the critical point of the liquid in such an investigation, since we can use stirring and purification and thus obtain ideal samples (with respect to the measurement accuracy). However, in investigations performed without mixing,[21] such a problem does arise. In solids, on the other hand, it becomes decisive.

2. In choosing between expressions (1) and (3), an important role is played by the separation of the regular part of the specific heat. Indeed, the phase transition is usually not connected with all the degrees of freedom of the system, and therefore formulas (1)–(3) pertain strictly speaking not to the total specific heat, but to the so-called singular part of the specific heat, i.e., the part affected by the phase transition. Thus, for transitions in ferromagnets, the specific heat of the lattice is usually insignificant, and for the critical point of a liquid it is possible to subtract the part corresponding to the degrees of freedom of the molecule of the ideal gas. The simplest method of taking into account the regular part is to impart to the constant B the meaning of a function of the temperature. Since the singular part is the function $T - T_c$, and the regular part is the function T, it is always possible in principle to consider relations in such a vicinity of T_c in which B is practically constant. But for imperfect samples the approach to T_c is limited by the smearing, and is of necessity small. Therefore, allowance for the dependence of B on T may turn out to be not a simple matter. This procedure can be readily employed in two cases.

If T_c of the solid is in the region of low tempera-

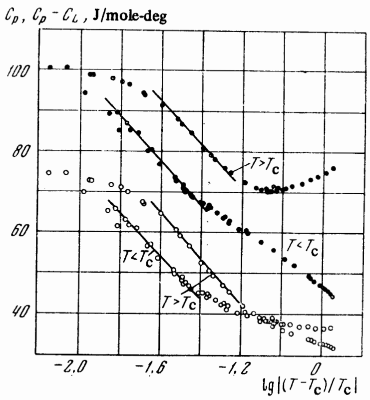

FIG. 6. Dependence of specific heat C_p (●) and $C_p - C_L$ (○) on log $|(T - T_c)/T_c|$ for single-crystal magnetite.

tures, the lattice specific heat is small and does not affect the form of the singularity, say, of the magnetic specific heat of a ferro- or antiferromagnet, even if we are unable to exclude it correctly (such a case was realized in [1,3]).

If T_c, to the contrary, is in the region of relatively high temperatures compared with the Debye temperature, then the lattice specific heat depends very little on the temperature (the Dulong and Petit law), and likewise has practically no effect on the form of the singular part, giving a constant shift of the entire curve of the specific heat (this case apparently takes place in [6]).

Unfortunately it is necessary to deal frequently with intermediate cases. The unknown dependence of the regular part of the specific heat on the temperature is superimposed on the singularity, and the resultant arbitrariness is the source of a distortion of the true relationships. Figure 6 shows simultaneously the experimental data on the total specific heat of single-crystal magnetite and on its singular part, obtained by subtracting the lattice contribution from C_p. The lattice part is subtracted in accordance with the usual procedure:[22]

$$C_L = D\left(\frac{\Theta_D}{T}\right) + 6E\left(\frac{\Theta_E}{T}\right).$$

According to the empirical data,[22] the Einstein temperature Θ_E is always larger than the Debye temperature Θ_D. The value $\Theta_E = \Theta_D$ used by us corresponds to the limiting case of the largest contribution of the Einstein function $E(\Theta_E/T)$ to the lattice part of the specific heat. The value $\Theta_D = 585°K$ is taken on the basis of [23]. For the transition temperature we assumed arbitrarily $T_c = 104.6°K$, which ensures parallelism of the logarithmic parts of the specific-heat curves on the right and on the left ($A_- = A_+$). It is clearly seen that although such an allowance for the lattice contribution is not strongly reflected in the values of the coefficients A_+ and A_-, the magnitude of the jump of the specific heat ΔC_p does change. Some change takes place also in the form of the curve and in the region of the logarithmic sections. Thus, allowance for the regular part is not always trivial in its influence on the element of the characteristics of the singularity when satisfaction of (1) and (2) is assumed.

In verifying the applicability of (3), an additional constant α appears, which is essentially determined by the choice of the value of B. Figure 7 shows data of the specific heat of nitrogen near the critical point,[13] represented in accordance with formula (3) for different arbitrary values of B. We see that in this case the curves plotted in a logarithmic scale have different slopes, corresponding to different values of α. The arbitrariness for formula (3) becomes quite complete if we assume further a certain temperature dependence of B (see above).

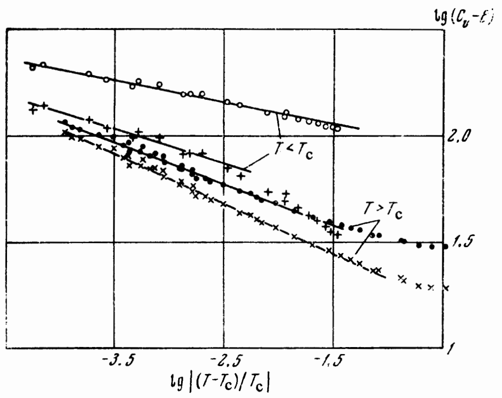

FIG. 7. Dependence of the specific heat $C_V - B$ of nitrogen on the temperature: ○ – B = 0.5 R, α = 0.10; * – B = +8.5 R, α = 0.16; ● – B = –0.5R, α = 0.20; X – B = +1.68 R, α = 0,24

3. COMPARATIVE CHARACTERISTICS OF THE SINGULARITIES OF THE SPECIFIC HEATS OF VARIOUS SUBSTANCES

For the reasons described above, we shall disregard completely formula (3) for solids. Variants of the formula (1) with $A_+ = A_-$ and $A_+ \neq A_-$, at the present status of samples, can be regarded as equally probable. Since the criterion for the selection of T_c has not yet been formulated, we shall choose T_c in order to carry out the analysis from a unified point of view in such a way as to satisfy formulas (1) and (2), and we shall henceforth assume that their satisfaction is arbitrary. The constants $A_\pm$ and $B_- - B_+) = \Delta C$ for a number of substances are listed in Table I for such a choice of T_c.

In this table we arranged the substances by groups of close physical properties: 1) liquid-vapor critical points of simple substances, 2) Heisenberg ferromagnets, 3) antiferromagnets, and 4) other cases of transitions. The fourth group includes the λ transition in liquid helium, which is in a class by itself, and phase transitions of the ordering type in magnetite Fe_3O_4 and in vanadium deuteride. The specific heat of the latter was measured for a powdered sample and is shown in Fig. 8. Unfortunately, the investigated sample was not of stoichiometric composition ($VD_{0.8}$), and this (see Sec. 1, Part 1) in conjunction with the inhomogeneity has led to a smearing of the peak in the immediate vicinity of T_c. However, the reliability with which the constants $A_\pm$ and ΔC were determined for this substance is not lower than for other solids in the sample.

We note that if we assume that formula (1) is valid, a subjective processing of the results can lead to a change of 10–20% in the value of A and 15–30% in ΔC (see Fig. 6). Stipulating (1) when (3) is actually valid or when $A_+ \neq A_-$ can lead to a deviation of $A_\pm$ by 50–

Table I.

Substance	T°_c, K	$A^*_\pm$	ΔC *	$\Delta C/A_\pm$
He^3 [24]	3,34	0,37	2,2	5,9
He^4 [24]	5,2	0.62	3.6	5,8
N_2 [13]	126,16	2,0	11,0	5.5
Ar [12]	150.67	2,2	11,5	5,2
O_2 [11]	154	2,4	11.0	4.6
Ni [6]	620	0.2	0.32	1.6
Co [6]	1376	0,3	0,65	2,2
Fe [6]	1043	0,72	1,0	1,4
$CuK_2Cl_4 \cdot 2H_2O$ [3]	0.89	0.2	0,38	1,9
Gd [9]	292	0.4	1.85	4,6
Dy [20]	175,3	0,68	3,0	4.4
MnF_2 [4] **	67,33	0,5	2,1	4,2
He^4 [25]	2.17	0,64	2,5	3,9
Fe_3O_4	104,6	2.8	1,8	0,6
VD	232,8	3,3	3,0	0,9

* The coefficient $A_\pm$ and the specific-heat jump of Δc are expressed in units of the gas constant R = 8.314 J/mole-deg.

** The values of A given in [4] are in error. This is clearly seen from a comparison of [4,26,27].

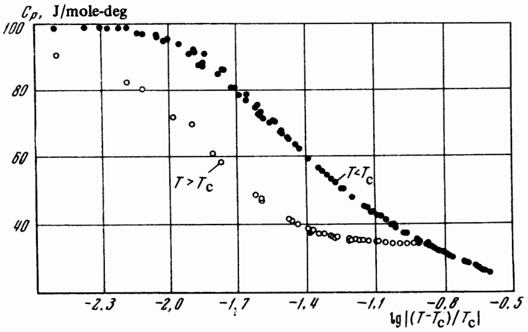

FIG. 8. Dependence of the specific heat C_p of vanadium deuteride on log $|(T - T_c)/T_c|$.

80% from A_- or A_+. Yet in many substances there are properties that differ by one order of magnitude in the coefficient $A_\pm$. Thus, the characteristics of the singularities are subject to objective quantitative differences that exceed the possible errors greatly.

Thus, in the first group of substances of the table we see a sharp decrease of the coefficient A_+ with decreasing temperature T_c in the case of the quantum liquids He^4 and He^3. This decrease was predicted by Yang,[28] who noticed that the quantum effects should lead to a smearing of the differences between empty and filled lattice points of the lattice gas. Confirmation of this prediction is evidence in favor of the correspondence between the liquid–vapor critical points of simplest substances to the model of the lattice gas. For solids, the analog is the Ising model. A similar smearing in the Ising model corresponds apparently to the appearance of additional possible spin positions in addition to the two opposite positions. The freest spin position is that of ordinary ferromagnets, which in accordance with this model are called Heisenberg ferromagnets. From the table we see that such ferromagnets actually have very low values of $A_\pm$ (second group of substances), similar to quantum liquids.

On the other hand, VD and to a certain degree Fe_3O_4[29] have transitions of the ordering type in hours. Vaks and Larkin[30] have shown that usual transitions of the order type in binary alloys can be regarded as corresponding Ising models. The values of the coefficients $A_\pm$ in these two substances are the largest in the table and are close to the values of A_+ for classical gases at the critical vapor–liquid points, which can be considered on the basis of the lattice-gas model which is analogous to the Ising model.

We are thus able apparently to judge the degree of correspondence of the Ising-model system by using the results of a phenomenological experiment.

Great interest attaches to the ratio $\Delta C/A_\pm$ which is given in the last column of the table. In the case when the assumption $A_+ = A_-$ holds true, this quantity is a dimensionless parameter, which greatly characterizes the feature of the specific heat at the transition point. We see that in spite of the large range of variation of A_+ and ΔC (one order of magnitude), the quantity $C/A_\pm$ remains constant within the group of substances, accurate to ~20–30%. It is curious that according to this attribute the λ point of He^4 is close to antiferromagnets. As shown by Vaks and Larkin,[30] the λ transition in He^4 reduces to a phase transition of the antiferromagnetic type in a lattice of the Ising type, but made up of flat dipoles. The value of $A_\pm$ for He^4 is also close to the antiferromagnet group in which we, like Belov,[31] include also gadolinium.

Of course, if $A_+ \neq A_-$, then $\Delta C \to \infty$, and the quantity $\Delta C/A_\pm$ becomes meaningless, but we cannot ascertain at present which of the assumptions is realized. It is possible that for different objects both are realized. Only further investigations can resolve this question. All the values of the quantities in the table have, unfortunately, a very low accuracy, owing to the unreliability of the initial data. The same unreliability is also the

Table II. Specific heat of single-crystal magnetite (J/mole-deg) in the region of the low-temperature transition.

T, °K	C_p	T, °K	C_p	T, °K	C_p	T, °K	C_p	T, °K	C_p	T, °K	C_p
85,672	44,42	93,206	60.81	101.161	70,08	103.508	94.42	107.239	91,59	113,801	70.56
86,121	44,96	98.857	62.77	101.208	71,72	103.971	97,54	107.750	88,09	114,045	71.46
86.868	45,69	98.926	62,22	101,233	70.89	104,246	97,14	107.908	86,89	114,374	70,59
87,416	46.34	99,161	63.81	101,486	72.85	104,430	99,36	108,279	84.57	114.397	70,83
87,886	46.61	99,321	63.71	101.523	73.63	104.886	99.71	108.831	80.95	114,432	70.85
88,350	47.12	99.644	64.92	102.035	76.89	105,218	100.68	109.214	79,14	115.034	70,83
89,333	48,03	99.977	66.20	102,245	80.40	105.342	100.38	109,404	78,12	115.355	71,05
89,853	48,81	100.057	66,66	102.335	80.14	105.495	100.55	109.997	76,03	116.269	71,69
90,326	49.24	100.112	66.20	102,534	83.64	105,771	98,85	110.371	74.79	117.602	72,34
92,496	52,01	100,337	67.23	102.589	84.65	105,801	98.85	111.417	72.29	118,935	73,33
93,781	53.67	100,503	67,34	102,761	85.44	106.094	97,99	112,269	71.13	120.271	74,00
95,055	55.74	100.865	68,49	102,835	86,99	106,269	97.43	112,829	70,64	121.643	75,06
96,351	57,79	100,901	68,95	102.997	85.38	106.414	96,41	113,314	70.64	123,014	76,24
97,486	59,78	100.919	69,40	103,030	89,69	106,745	94.13	113.411	70,37		
97,626	60,53	101,083	70.30	103.144	89.37	106,741	94.25	113,606	70,35		

Table III. Specific heat of $VD_{0.8}$ (J/mole-deg) in the phase-transition region.

T, °K	c_p	T, °K	c_p	T, °K	c_p	T, °K	c_p	T, °K	c_p	T, °K	c_p
179,081	26,84	209.199	38,55	225,034	65.02	229.483	90,72	235.762	69.82	251,257	35.01
181,164	27,28	209.348	38.34	225.069	65.72	229,786	90,90	236,463	61,20	251.597	34,97
182.112	27,42	210.339	39.12	225,506	66 84	229,948	90.54	236.780	58.30	253.161	34.79
182,580	27.67	210,691	39.96	225,545	67,68	229.815	92.04	238,349	48.71	254,790	34.73
186,209	28,48	211.311	40.05	225,657	67,48	230.226	93.80	238.707	47,82	256.421	34.62
186.657	28,79	212,293	41.16	226.054	70.11	230.503	95.12	238,724	47.13	258,051	34,56
187.506	28.89	213.227	42.29	226,148	70,32	230.615	94.60	240.569	41,43	259,680	34,66
192.758	30.25	213,658	42.12	226.370	68,96	230.750	95.70	240.698	41.03	261.305	34.52
194.219	30.70	213.914	42.31	226.730	71.12	230.774	96,61	240.754	41.09	263.749	34.65
195,489	31,00	213.978	42.57	226.938	72,20	231,040	96.94	242.083	38.70		
196,731	31,59	214.933	43.88	226.820	73.18	231.132	97,23	242,441	38.18	164.467	24.17
197.969	32.05	215.152	43.81	227.050	72.61	231.306	98.81	242,601	38,26	170.433	25,14
198.422	32,01	215,837	45.05	227,092	75,38	231,412	98.51	243,536	37,28	174.171	25,84
198,746	32,49	216.349	45.49	227.262	74,46	231,571	98,87	243.704	37.21	174,667	25,94
199,627	32,68	218.255	48.04	227,725	76,82	231,667	99.10	244,614	36,75	178.539	26.65
200.266	32.97	219.351	50.42	227.711	78.66	231.827	98.93	244.657	36,62	198.776	32.37
200,472	33.28	219.659	50.47	228.056	78.25	232.092	98.72	244.997	36.16	199.767	32,31
200.816	33,27	220.406	52.44	228.256	80,38	232.359	96.61	245.266	36.41	214.109	51.99
201,178	33,41	220,865	53,30	228,417	80,68	232.585	96.55	246.805	35.89	241.184	40.04
202.159	34,09	221.404	54.63	228,727	85,82	232.784	94,58	246.802	35.77	242,161	37.54
223.130	34.37	221.993	55,72	228,803	85.54	233.067	93.37	247,046	35.69		
204.162	34.93	222.374	57.06	228.992	84.62	233.525	90,86	247,905	35.73		
205.045	35,47	223.306	59.69	229.368	86.90	234.302	82.31	248,388	35.44		
207,804	37.33	224,198	62.31	229,524	88.06	234.563	80.43	249,027	35,38		
208,338	37.45	224.560	63.57	229.662	87.26	235,291	71.77	249.988	35.17		

reason why certain results[2,5] were not used by us. The data of Skalyo and Friedberg,[1] although reliable, pertain to a layered antiferromagnet and we still do not know how to compare two-dimensional and three-dimensional structures. Thus, Table I apparently contains a sufficiently complete and weighted summary of data on the characteristics of the singularities at the transition points.

Insofar as we know, the data and the specific heat of VD are published here for the first time, and the data on the specific heat of magnetite in the region of the low-temperature transition[32] are obsolete. We therefore present detailed values of the specific heat for these these substances in Tables II and III.

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[1] J. Skalyo and S. A. Friedberg, Phys. Rev. Lett. **13**, 133 (1964).

[2] T. Shinoda, H. Chihara, and S. Seki, J. Phys. Soc. Japan **19**, 1637 (1964).

[3] A. R. Miedema, R. F. Wielinga and W. J. Huiskamp, Phys. Lett. **17**, 87 (1965).

[4] D. T. Teaney, Phys. Rev. Lett. **14**, 898 (1965).

[5] W. K. Robinson and S. A. Friedberg, Phys. Rev. **117**, 402 (1960).

[6] Ya. A. Kraftmakher and T. Yu. Romashina, Fiz. Tverd. Tela **8**, 1966 (1966) [Sov. Phys.-Solid State **8**, 1562 (1966)].

[7] M. E. Fisher, Phys. Rev. **136**, A599 (1954).

[8] P. G. Strelkov, E. S. Itskevich, V. N. Kostryukov, G. G. Mirskaya, and B. N. Samoilov, ZhFKh (J. of Phys. Chem.) **28**, 459 (1964).

[9] A. V. Voronel', S. R. Garber, A. P. Simkina, and I. S. Charkina, Zh. Eksp. Teor. Fiz. **49**, 429 (1965) [Sov. Phys.-JETP **22**, 301 (1966)].

[10] V. M. Mamnitskiĭ, PTÉ, No. 2, 193 (1967).

[11] A. V. Voronel', V. A. Popov, V. G. Simkin, and Yu. R. Chashkin, Zh. Eksp. Teor. Fiz. **45**, 828 (1963) [Sov. Phys.-JETP **18**, 568 (1964)].

[12] A. V. Voronel', V. G. Snigirev, and Yu. R. Chashkin, Zh. Eksp. Teor. Fiz. **48**, 981 (1965) [Sov. Phys.-JETP **21**, 653 (1965)].

[13] A. V. Voronel', V. G. Gorbunova, Yu. R. Chashkin, and V. V. Shchekochikhina, Zh. Eksp. Teor. Fiz. **50**, 897 (1966) [Sov. Phys.-JETP **23**, 597 (1966)].

[14] A. V. Voronel' and Yu. R. Chashkin, Zh. Eksp. Teor. Fiz. **51**, 394 (1966) [Sov. Phys.-JETP **24**, 263 (1967)].

[15] Yu. R. Chashkin, V. G. Gorbunova, and A. V. Voronel', Zh. Eksp. Teor. Fiz. **49**, 433 (1965) [Sov. Phys.-JETP **22**, 304 (1966)].

[16] Yu. R. Chashkin, A. V. Voronel', V. A. Smirnov, and V. G. Gorbunova, Zh. Eksp. Teor. Fiz. **52**, 112 (1967) [Sov. Phys.-JETP **25**, 72 (1967)].

[17] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika, Nauka, 1964 [Statistical Physics, Addison–Wesley, 1958].

[18] B. A. Strukov, Fiz. Tverd. Tela **6**, 2862 (1964) [Sov. Phys.-Solid State **6**, 2278 (1965)].

[19] A. V. Voronel' and M. Sh. Giterman, Zh. Eksp. Teor. Fiz. **39**, 1162 (1960) [Sov. Phys.-JETP **12**, 809 (1960)].

[20] M. Griffel, R. E. Skochdopole, and F. H. Speadding, J. Chem. Phys. **25**, 75 (1956).

[21] C. Edwards, J. A. Lipa, and M. J. Buckingham, Phys. Rev. Lett. **20**, 496 (1968).

[22] R. Venner, Thermochemical Calculations (Russ. transl. IIL, 1950).

[23] M. Dixon, F. E. Hoare, and T. M. Holden, Phys. Lett. **14**, 184 (1965).

[24] M. R. Moldover and W. A. Little, Phys. Rev. Lett. **15**, 54 (1965).

[25] M. J. Buckingham and W. M. Fairbank, Prog. in Low Temperature Physics, ed. by Gorter, N. Holland Publishing Company, Amsterdam (1961).

[26] D. T. Teaney, V. L. Moruzzi, and B. E. Argule, J. of Appl. Phys. **37**, 1122 (1966).

[27] M. I. Bagatskiĭ, A. V. Voronel', and V. G. Gusak, Zh. Eksp. Teor. Fiz. **43**, 728 (1962) [Sov. Phys.-JETP **16**, 517 (1963)].

[28] C. N. Yang and C. P. Yang, Phys. Rev. Lett. **13**, 303 (1964).

[29] K. P. Belov, Magnitnye prevrashcheniya (Magnetic Transformations), Fizmatgiz, 1959.

[30] V. G. Vaks and A. I. Larkin, Zh. Eksp. Teor. Fiz. **49**, 975 (1965) [Sov. Phys.-JETP **22**, 678 (1966)].

[31] K. P. Belov and A. V. Ped'ko, Zh. Eksp. Teor. Fiz. **42**, 87 (1962) [Sov. Phys.-JETP **15**, 62 (1962)].

[32] R. W. Millar, JACS **51**, 215 (1929).

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