EFFECT OF SAMPLE INHOMOGENEITY ON SOME PROPERTIES OF THE SPECIFIC-HEAT SINGULARITY DURING PHASE TRANSITIONS CLOSE TO TRANSITIONS OF THE SECOND KIND

B. Ya. SUKHAREVSKIĬ, A. V. ALAPINA, Yu. A. DUSHECHKIN, T. N. KHARCHENKO, and I. S. SHCHETKIN

Physico-technical Institute for Low Temperatures, Ukrainian Academy of Sciences

Submitted September 25, 1969

Zh. Eksp. Teor. Fiz. 58, 1532–1542 (May, 1970)

The effect of inhomogeneity on the character of the specific-heat singularity is investigated by considering an example of powdered synthetic magnetite. Experimental data are interpreted in terms of a model of the sample in which the latter is regarded as the sum of homogeneous and practically noninteracting volumes. Some formulas are put forward which can be used to deduce from experimental data some of the parameters characterizing the specific-heat singularity during a phase transition of the second kind in an inhomogeneous sample. These include the mean critical temperature τ_m, the transition range, the degree of transition smearing, the specific heat jump, and the magnitude and direction of the shift of the peak relative to τ_m. Analysis of the experimental data reported here and those taken from the literature[1] has confirmed the validity of this interpretation.

1. INTRODUCTION

THE singularities in the physical properties of materials during phase transitions close to transitions of the second kind in crystals are usually investigated using imperfect and insufficiently homogeneous samples. The observed singularities are then found to be smeared out to a greater or lesser extent. Nevertheless, experimental results including, in particular, data on the specific heat are analyzed by traditional methods, i.e., by plotting $\ln|(T - T_C)/T_C|$ or $\ln C$ against $\ln|(T - T_C)/T_C|$, where T_C is chosen in accordance with the criteria governed by the ideology of the particular author. The subjective nature of the choice of T_C has been discussed in some detail by Voronel' et al.[1]

The value of T_C used in the analysis of experimental data is usually different from the position of the peak, which may not be the same for different physical properties of a given specimen. This fact throws some doubt on whether the concept of the Curie point can be uniquely defined.

It is possible, however, to assume that the inhomogeneity of the specimens is at least one of the main reasons for these difficulties. Specimen inhomogeneity was taken into account by Mikulinskiĭ[2] within the framework of the phenomenological Landau theory, but this does not allow quantitative comparison with experiment.

The effect of inhomogeneity on the smearing out of the specific heat singularity was discussed qualitatively in[1]. Voronel'[3] has reported quantitative estimates for the case where the inhomogeneity was due to the hydrostatic effect near the critical point. The effect of inhomogeneity was explained in[4] by the smoothing out of the specific-heat jump during the transition to the superconducting state.

2. EXPERIMENT

To establish the influence of inhomogeneity on the specific-heat singularity in the region of the phase transition, we have used the data of our own experiments on the specific heat of magnetite (Fe_3O_4) specimens in the form of large-grain powder with maximum grains size of about 1 mm.

This medium is convenient because it can be synthesized from very pure initial material with total impurity concentration not exceeding 0.1%. The synthesis is carried out by ceramic technology ensuring sufficient quality and homogeneity of the specimens. Heat treatment can be used to obtain the specimens with given density of structural cation vacancies,[5] which are known[6] to have a considerable effect on the ordering temperature of di- and trivalent iron atoms in the octahedral positions of the crystal lattice of magnetite (Fd3m). It follows that even a slight inhomogeneity in the distribution of structural vacancies may lead to an appreciable smearing out of the transition. At the same time, the relatively small total number of defects means that each magnetite crystallite may be regarded as more or less perfect.

The magnetite specimens which we have examined have ~1 and ~4 at.% structural vacancies in the octahedral positions according to x-ray and chemical analyses, respectively.[1)]

The temperature dependence of the specific heat of the specimens in the temperature range 12–160°K is shown in Fig. 1. The specific heats were measured with the adiabatic vacuum calorimeter.[7] The sufficiently high accuracy of the measurements (experimental un-

[1)]We are indebted to I. I. Vishinevskiĭ, B. G. Alapin, and L. A. Pavlov for placing these specimens at our disposal and for carrying out the x-ray and chemical analyses.

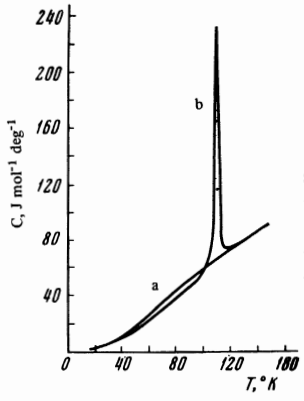

FIG. 1. Specific heat of magnetic specimens with different density of structural vacancies as a function of temperature. a) Density of vacancies ~4 at. %; b) density of vacancies ~1%.

certainty not exceeding 0.3%) is ensured by strictly adiabatic conditions which eliminate the "temperature drift" so that no additional errors are introduced by corrections for heat transfer. This is particularly important in the region of the phase transformation where the time for the establishment of thermal equilibrium after the specimen heater is switched on may reach a few hours, and the size of the temperature step is quite small (0.04—0.06 deg). Curve a in Fig. 1 refers to a specimen with a high density of vacancies and shows no specific-heat singularity. Since x-ray analysis reveals no differences in the properties of this specimen at room and liquid nitrogen temperatures, it would appear that ordering does not occur for vacancy densities of ~4 at.%. A sharp specific heat anomaly corresponding to a phase transition into an ordered state is observed on curve b in Fig. 1 (density of vacancies ~1 at.%) at temperatures between 105 and 115°K.

We note that, for a magnetite specimen with 1% of vacancies, x-ray analysis at liquid nitrogen temperatures show that there are differences at large angles which can be explained by changes in symmetry during the phase transition.[8]

Figure 2 shows in greater detail the shape of the specific-heat singularity. In a series of experiments the specimen was cooled down to 78°K and this was followed by continuous measurements throughout the temperature range of the singularity. In another series of experiments the specimen was cooled down to some given temperature in this interval (105—115°K), and the presence of hysteresis would have led to a readily detectable shift of the experimental points because of the sharp temperature dependence of the specific heat in this region.

The disposition of the points in Fig. 2 indicates the absence, to within experimental error (~0.01°), of any appreciable hysteresis. This enables us to assume that the transformation which we are considering is close to a phase transformation of the second kind.

The fact that we have experimental data for a magnetite specimen which has not undergone transition to the ordered state facilitates the isolation of the regular part of the specific heat C_L. In the region of the high-temperature phase of the specimen with the lower density of vacancies we can use the corresponding region of curve a (Fig. 1) for C_L. In the low-temperature phase, C_L may be taken into account by extrapolating the regular part of curve b (Fig. 1) into the

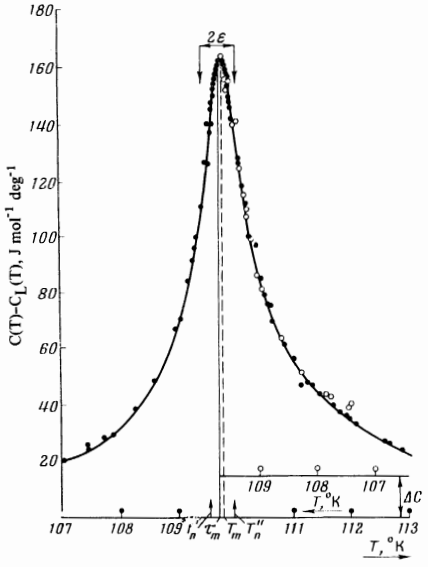

FIG. 2. Specific heat of magnetite in the region of the singularity as a function of temperature: ●—experimental values; ○—mirror reflection in τ_m and values of the specific heat on the left-hand branch shifted by ΔC.

region of the singularity. This extrapolation is best carried out by using the temperature dependence of the effective Debye temperature (see Fig. 3), which was determined by comparing the experimental curve C(T) with the tabulated values of the Debye specific-heat function.

3. QUANTITATIVE ESTIMATES OF THE EFFECT OF INHOMOGENEITY

To interpret our data we have used a model similar to that adopted in[4]. It was assumed that the specimen consisted of a set of homogeneous volumes, each of which had its own Curie temperature τ which depended on the density of impurities, vacancies, and other crystal-structure defects. In this way, each homogeneous volume in the inhomogeneous specimen was treated as nonideal. These volumes are small in comparison with the specimen, so that the distribution function $(\partial x/\partial \tau)d\tau$ which describes the relative amount of material with the Curie temperature between τ and $\tau + d\tau$ can be regarded as continuous. They should be sufficiently large to ensure that the interactions between them can be neglected. This model appears to be valid for a powdered specimen in which each crystallite forms a homogeneous volume. However, in the case of monolithic objects, there may be difficulties due to the fact that, at temperatures close to the value of τ for a given homogeneous volume, the correlation radius may exceed its linear dimensions.

All the calculations carried out below can be performed for a specific heat having a symmetric logarithmic singularity near $T_C = \tau$ in each homogeneous volume:

$$C = -A \ln t + B_-, \quad T < \tau,$$
$$C = -A \ln t + B_+, \quad T > \tau, \tag{1}$$

where $t = |T - \tau|/\tau$. It will be assumed that the values

of A and B_+, B_- are the same for all the homogeneous volumes in the specimen.

Assuming that the departure of the Curie points of the individual homogeneous volumes from the mean value is due to random factors (for example, inhomogeneity in the chemical composition), it is convenient to represent $\partial x/\partial\tau$ approximately at the Gauss function as in[9]. However, since the distribution function is used only in expressions of the form

$$\int \frac{\partial x}{\partial \tau} C(T,\tau)\,d\tau$$

which represents the convolution operation, it follows that in view of the well-known properties of convolution[10] the Gaussian distribution can be replaced without loss of accuracy by another similar function.

To simplify the calculations we have replaced the function $\partial x/\partial\tau$ by an equilateral triangle of height $1/\epsilon$ at $\tau = \tau_m$ and a base length of 2τ. This model appears to correspond to our samples, since we are justified in assuming that each crystallite is homogeneous and there is no appreciable interaction between the crystallites. Moreover, the inhomogeneity of the specimen is largely due to differences in the nonstoichiometry of the individual grains-crystallites. The departure of nonstoichiometry (density of structural vacancies) from the mean value is most likely to be symmetric, since the inhomogeneity of the magnetite specimen with 1% structural vacancies is relatively low (this is indicated by the relatively sharp and high specific-heat peak), and we may expect that the assumed symmetric shape of the function $\partial x/\partial\tau$ will be valid and that the values of A and B_+, B_- in Eq. (1) will be nearly the same for all the homogeneous volumes of the specimen. For $\tau \le \tau_m - \epsilon$ and $\tau \ge \tau_m + \epsilon$ we have $\partial x/\partial\tau = 0$. The specific heat of the specimen is given by

$$C(T) = A\left\{\int_0^T \frac{\partial x}{\partial\tau}\ln(T-\tau)\,d\tau + \int_T^\infty \frac{\partial x}{\partial\tau}\ln(\tau-T)\,d\tau - \int_0^\infty \frac{\partial x}{\partial\tau}\ln\tau\,d\tau\right\} + B_+ + x(T)(B_- - B_+), \tag{2}$$

where x(T) is the relative amount of the low-temperature phase at temperature T. The expression obtained by evaluating the integrals in Eq. (2) leads to the following results:

$$\text{(a)}\ \left.\frac{dC}{dT}\right|_{T=\tau_m-\varepsilon} > 0; \quad \left.\frac{dC}{dT}\right|_{T=\tau_m+\varepsilon} < 0; \quad \left.\frac{dC}{dT}\right|_{T=\tau_m} = \frac{B_+ - B_-}{\varepsilon}. \tag{3}$$

Thus, depending on the sign of $B_+ - B_-$, the extremum of C(T) lies to the right or left of τ_m;

$$\text{(b)}\qquad \left.\frac{d^2C}{dT^2}\right|_{T\to\tau_m} < 0. \tag{4}$$

The condition $d^2C/dT^2 = 0$ defines the points of inflection on the C(T) curve:

$$T_n' = \tau_m - \frac{\varepsilon\sqrt{\alpha}}{\sqrt{\alpha+1}} \qquad T_n'' = \tau_m + \frac{\varepsilon}{\sqrt{\alpha+1}}, \tag{5}$$

where

$$\alpha = \exp\{(B_- - B_+)/A\}; \tag{6}$$

(c) at the points of inflection we have

$$\left.\frac{dC}{dT}\right|_{T=T_n'} > 0; \quad \left.\frac{dC}{dT}\right|_{T=T_n''} < 0. \tag{7}$$

Moreover,

$$\left.\frac{dC}{dT}\right|_{T=\tau_m-\alpha\varepsilon/(\alpha+1)} = \frac{A}{\varepsilon}\frac{2\alpha+1}{\alpha+1}\ln\frac{2\alpha+1}{\alpha} > 0,$$

$$\left.\frac{dC}{dT}\right|_{T=\tau_m+\varepsilon/(\alpha+1)} = -\frac{A}{\varepsilon}\frac{\alpha+2}{\alpha+1}\ln(\alpha+2) < 0, \tag{8}$$

so that when $B_+ - B_- > 0$ the extremum lies in the range $(\tau_m, \tau_m + \epsilon/(\alpha+1))$, whereas for $B_+ - B_- < 0$ it lies in the range $(\tau_m - \alpha\epsilon/(\alpha+1), \tau_m)$. Since both intervals lie between the points of inflection, where $d^2C/dT^2 < 0$, the specific-heat extremum is, in fact, a maximum. The approximate position T_m of the maximum of $C(\tau)$ can be found by linear interpolation between extreme points of these two intervals:

$$T_m \approx \tau_m - \varepsilon\frac{\alpha\ln\alpha}{(1+2\alpha)\ln(1+2\alpha) - \alpha\ln\alpha} \tag{9}$$

For $B_= - B_- < 0$ ($\ln\alpha > 0$), and

$$T_m \approx \tau_m - \varepsilon\frac{\ln\alpha}{(\alpha+2)\ln(\alpha+2) - (\alpha+1)\ln\alpha} \tag{9'}$$

for $B_+ - B_- > 0$ ($\ln\alpha < 0$). These two equations were obtained for a special form of the analytic dependence of the singularity as given by Eq. (1) and, therefore, the shift of the maximum relative to τ_m is determined by this relation. Of course, for other physical properties showing a singularity and measured on the same specimen the shift relative to τ_m will, in general, be different because of the difference in the analytic expression for the singularity. Moreover, the difference between the positions of the extrema in these physical properties will increase with increasing smearing of the transition due to the sample inhomogeneity.

Outside the region $(\tau_m - \epsilon, \tau_m + \epsilon)$ the specific heat is described by an expression of the form

$$C_\mp(t) = -A\ln t + \begin{Bmatrix} B_- \\ B_+ \end{Bmatrix} + f(t,\delta), \tag{10}$$

where

$$t = \left|\frac{T-\tau_m}{\tau_m}\right|, \qquad \delta = \frac{\varepsilon}{\tau_m}, \qquad t > \delta,$$

$$f(t,\delta) = -\frac{A}{2\delta^2}\{(t-\delta)^2\ln(t-\delta) + (t+\delta)^2\ln(t+\delta) - 2(t^2+\delta^2)\ln t - (1-\delta)^2\ln(1-\delta) - (1+\delta)^2\ln(1+\delta)\}. \tag{11}$$

The temperature dependence of the specific heat in the interval $(\tau_m - \epsilon, \tau_m + \epsilon)$ is shown by Eq. (2) to be of the form

$$C_\mp(t) = -A\ln t + \begin{Bmatrix} B_- \\ B_+ \end{Bmatrix} + \varphi(t,\delta), \tag{12}$$

where $t < \delta$, and

$$\varphi(t,\delta) = -\frac{A}{2\delta^2}\{(\delta-t)^2\ln(\delta-t) + (t+\delta)^2\ln(t+\delta) - 2(t^2+\delta^2)\ln t - (1-\delta)^2\ln(1-\delta) - (1+\delta)^2\ln(1+\delta) \mp (\delta-t)^2\ln(1/\alpha)\}. \tag{13}$$

The function f(t, δ) does not depend very much on the temperature, and when $t > 2\delta$ it varies between 0.52A and 0.50A. When $t < 2\delta$ the function f(t, δ) at first appreciably increases and then decreases. For example,

$$f(\delta,\delta) = \varphi(\delta,\delta) = 0.6A,$$
$$\varphi(0.5\delta,\delta) = (0.76 \mp 0.13\ln\alpha)A,$$
$$\varphi(0.25\delta,\delta) = (0.43 \mp 0.28\ln\alpha)A. \tag{14}$$

The negative sign refers to the region $T < \tau_m$, and the positive sign to the region $T > \tau_m$.

The formula given by Eq. (10) differs from Eq. (1) by a term which is constant right up to $t \sim \delta$ with T_C replaced by τ_m (the mean temperature for the transition interval). Its value is shifted relative to the specific-heat peak in the direction determined by the sign of $B_- - B_+ = \Delta C$. The magnitude of the shift can be estimated from Eq. (9). The parameter ϵ which is a measure of the smearing of the transition can be found from Eq. (5), using experimental data on the points of inflection of the specific heat curve. For transitions that are not too smeared out ($2\epsilon/\delta T \ll 1$, where δT is the temperature range in which there is a logarithmic singularity and outside which the systematic departure of the experimental points from the C, log T straight line exceeds the spread), the height of the specific-heat peak is not very different from its value at τ_m, and can be represented approximately by the following relation which is a consequence of Eq. (12):

$$C(T_m) \approx C(\tau_m) \approx -A \ln \delta + 2A(1 + {}^1/_4 \ln \alpha), \qquad (15)$$

This shows that the height of the maximum decreases with increasing transition width.

Estimates based on Eqs. (5), (9), and (15) cannot pretend to high accuracy because in addition to the possible correlation between the individual homogeneous volumes for $t < \delta$, which were noted at the beginning of this paper, there is an effect associated with the nonideal nature of each of these volumes and, consequently, one should, strictly speaking, use a function which is smoother than Eq. (1) in Eq. (2). Hence it follows that Eq. (12) leads to a specific heat which is probably somewhat too high.

The results for $t > \delta$ seem more accurate, and this enables us to analyze the experimental data for a not too highly smeared out singularity in terms of the coordinates C and ln t in accordance with Eq. (10) and the above estimates of f(t, δ). It follows from Eq. (10) that

$$C_-(t) - C_+(t) = B_- - B_+ = \Delta C. \qquad (16)$$

This means that a mirror image in the τ_m line of one of the branches of the C(T) curve obtained by subtracting the regular part from the experimental curve should coincide with the second branch after a shift of ΔC along the C axis. The position of the axis of symmetry gives τ_m, and the shift along this axis gives ΔC. For the interval $(\tau_m - \epsilon, \tau_m + \epsilon)$ we have from Eq. (12)

$$\frac{C_+(t) - C_-(t) + \Delta C}{\Delta C} = \left(1 - \frac{t}{\delta}\right)^2, \qquad (17)$$

and this yields the following formula which is convenient for the analysis of the experimental data:

$$\sqrt{\frac{C_-(t) - C_+(t)}{\Delta C}} = \frac{t}{\delta} = \frac{T}{\varepsilon} - \frac{\tau_m}{\varepsilon}. \qquad (18)$$

4. DISCUSSION OF RESULTS

An analysis of the temperature dependence of the specific heat of magnetite in the region of the singularity, which is based on Eq. (16) (comparison of the two branches by mirror reflection and shift along the axis of symmetry), is shown in Fig. 2. The results are

$\tau_m = 109.72°$ K, $\Delta C = B_- - B_+ = -15$ J-mol^{-1}deg^{-1}

The direction of the shift relative to the maximum $T_m = 109.76°$K gives the sign of ΔC. We note that Eq. (16) was obtained on the assumption that

$$A(T < \tau) = A(T > \tau) \qquad (19)$$

in Eq. (1). The validity of Eq. (16) is illustrated by the right-hand side of Fig. 2, which appears to confirm this assumption.

The method enables us to determine not only the value $T_C = \tau_m$, but also it seems to us to lead to a no less satisfactory verification of Eq. (19) than is indicated by the parallelism of the linear parts of the graphs of C(t) against log t (Fig. 4) for which three close values of T_C were employed, namely: 109.66, 109.72, and 109.78°K. From Fig. 4b, for which $T_C = \tau_m = 109.72°$K we have $A = 48 \pm 0.5$ J mol^{-1}deg^{-1} and $\Delta C \approx -(15 \pm 4)$ J mol^{-1}deg^{-1}, which are in agreement with the values given above. We note the unusual sign of the discontinuity in the specific heat.

The use of the smooth function $C_L(T)$ for the isolation of the regular part as, for example, in[1] does not lead to any basic changes but simply increases the specific-heat jump by 5 J mol^{-1}deg^{-1}. The inflection points determined from Fig. 2, i.e., $T_n' = 109.55 \pm 0.03°$K and $T_n'' = 109.95 \pm 0.03°$K, enabled us to calculated from Eqs. (5) and (9) the following values: $\epsilon = 0.3 \pm 0.05°$K and $\tau_m = 109.73 \pm 0.03°$K. This value of τ_m is practically the same as that given above. It follows from the above estimates for Eq. (11) that graphs of the kind shown in Fig. 4 can be reliably plotted up to $t \sim \delta$. Accordingly, in our case, the linearity in Fig. 4b should extend up to $\log t \approx -2.6$ and this is, in fact, observed. This considerable width of the linear region along the log t axis is ensured by the sufficiently low degree of smearing ($2\epsilon/\delta T \approx 0.15$).

Analysis of the specific-heat data for magnetite given in[1] has enabled us to obtain the following parameters from the temperatures corresponding to the points of inflection, using Eqs. (5) and (9), and the value $A = 48$ J mol^{-1} deg^{-1}.

Monocrystalline specimen: $T_n' = 102.6°$K, $T_n'' = 107.4°$K, $T_m = 105°$K, $\epsilon = 3.4°$K, $\tau_m = 104.7°$K (the value $T_C = 104.6°$K was adopted in[1]); $2\epsilon/\delta T \approx 2$.

The region in which a linear (C, log t) graph could be constructed was restricted by the value $\log \delta = -1.5$, whereas the logarithmic singularity itself,

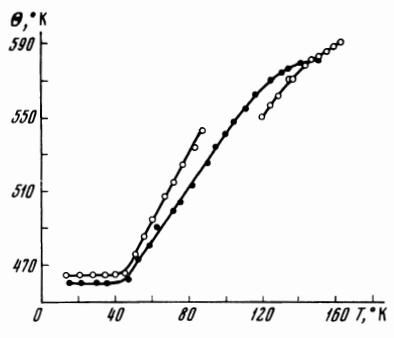

FIG. 3. Temperature dependence of the Debye temperature Θ_D on T for magnetite specimens: O—density of vacancies ~4 at. %; O—density of vacancies ~1 at. %.

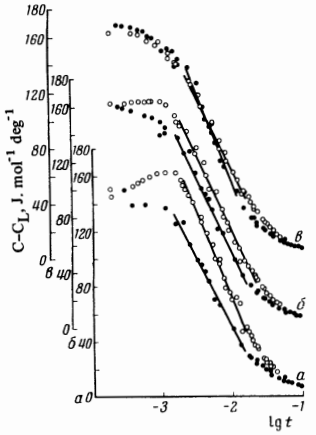

FIG. 4. Specific heat ($C - C_L$) as a function of log t for magnetite: a–τ_m = 109.66°K; b–τ_m = 109.72°K; c–τ_m = 109.78°K; ●–$T < \tau_m$, ○–$T > \tau_m$.

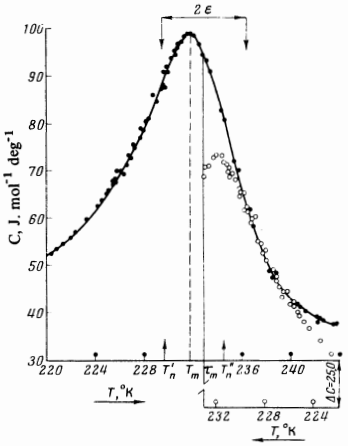

FIG. 5. Specific heat of vanadium deuteride [1] as a function of temperature in the region of the singularity. ●–experimental; ○–mirror reflection in τ_m and values of the specific heat on the left-hand branch shifted by ΔC.

judging by data obtained for our specimen (Fig. 4b), begins with log t ≈ −1.7 ($T > \tau_m$) and log t ≈ −1.8 ($T < \tau_m$). It follows that in the case of the monocrystalline magnetite in[1] and even more so for the polycrystalline specimen in the same paper, the region of linear dependence is absent from the semilogarithmic graph.

Polycrystalline specimen: $T_n' = 101.7°K$, $T_n'' = 112.9°K$, $T_m \approx 107°K$, $\tau_m = 106.2°K$, $\epsilon = 8°K$, $2\epsilon/\delta T \approx 5$, $\log \delta = -1.1$.

Let us now compare the values $C(\tau_m)$ for all three magnetite specimens: for our specimen $C_1(\tau_m) = 227$ J mol^{-1} deg^{-1}, for the monocrystalline specimen in[1] $C_2(\tau_m) = 100$ J mol^{-1}deg^{-1}, and for the polycrystalline specimen in[1] $C_3(\tau_m) = 80$ J mol^{-1} deg^{-1}.

From Eq. (15) we have

$$C_2 = C_1 - A\ln(\varepsilon_2/\varepsilon_1) = 109 \text{ J mol}^{-1}\text{ deg}^{-1}$$
$$C_3 = C_1 - A\ln(\varepsilon_3/\varepsilon_1) = 71 \text{ J mol}^{-1}\text{ deg}^{-1}$$

so that there is a definite quantitative correspondence between the height of the maximum and the smearing of the transition. The discrepancy between the values of τ_m for different magnetite specimens is not surprising because τ_m depends on the mean density of impurities and vacancies.

Detailed experimental data on the temperature dependence of the specific heat of vanadium deuteride are given in[1]. It follows from Fig. 8 in that paper that the specific-heat of this specimen is described by Eq. (1) in a sufficiently broad temperature range with $T_C = 232.8°K$, $A = 27.4$ J-mol^{-1}deg^{-1}, and $\Delta C = 25$ J-mol^{-1}deg^{-1}. Since the transition in vanadium deuteride is not too smeared out, it is possible to use the above method of the singularity branch reflection (Fig. 5). The values $T_C = \tau_m = 232.8°K$ and $\Delta C = 25$ J-mol^{-1}deg^{-1} obtained in this way are in agreement with these reported in[1]. From Eqs. (5) and (9), and the temperatures corresponding to the points of inflection and the position of the maximum, i.e., $T_n' = 229.7 \pm 0.1°K$, $T_n'' = 234.5 \pm 0.1°K$, $T_m = 231.8 \pm 0.1°K$, we find that $\epsilon = 3.5 \pm 0.2°K$, $\tau_m = 232.7 \pm 0.2°K$. The fact that for the vanadium deuteride specimen the degree of smearing $2\epsilon/\delta T \approx 0.25$ is sufficiently small but, at the same time, larger than for our own specimen of magnetite, enabled us to analyze the specific-heat data for the interval (τ_m, $\tau_m + \epsilon$) in accordance with Eq. (18). This analysis is simplified after the reflection operation: the numerator in Eq. (17) is equal to the difference between the ordinates in this interval. The construction shown in Fig. 6 indicates the validity of Eqs. (17) and (18), and provides us with the possibility of using a further method (slope and intercept on the ordinate axis) to show that $\epsilon = 3.5°K$ and $\tau_m = 232.9°K$.

Quantitative discrepancies in the region ($\tau_m - \epsilon$, $\tau_m + \epsilon$), due to the probable interaction between the homogeneous volumes and the particular shape of the $dx/d\tau$ function, were noted above. Our results show that this did not occur in the case of vanadium deuteride.

We note that in the powdered specimen of vanadium deuteride used in[1] there was, in addition, an inhomogeneity which was probably due to different deviation from stoichiometry in different grains. Therefore, the model proposed here may be assumed to be valid for vanadium deuteride just as it is valid for our magnetite specimen. The interval along the log t axis in which C should be a linear function of log t extends up to log t = log δ = −1.85, which is in agreement with the data in Fig. 8 of[1].

5. CONCLUSION

We have proposed an explanation of the smearing of specific-heat singularities corresponding to phase

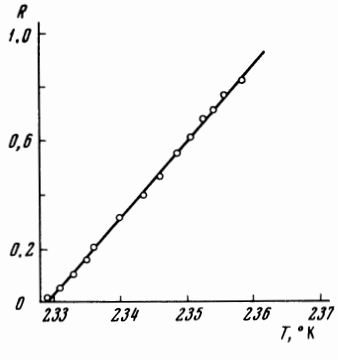

FIG. 6. The quantity $R = ([C_-(t) - C_+(t)]/\Delta C)^{1/2}$ in Fig. 5 as a function of temperature for vanadium deuteride [1] in the region (τ_m, $\tau_m + \epsilon$).

transitions of the second kind. This is based on the assumed inhomogeneity of imperfect specimens. Formulas have been derived which can be used to find the interrelation between the main parameters describing the specific heat in the transition region, namely, points of inflection, shift of the maximum relative to the mean Curie temperature τ_m, the specific heat jump, and the smearing interval.

An analogous calculation can readily be carried out for other physical properties, so that the inhomogeneity can be used to explain not only the magnitude and direction of the shift of extrema relative to $T_C = \tau_m$, but also the differences in the positions of the singularities in different physical properties of the same specimen.

We note that our calculations were based on two types of assumption. Assumptions of the first kind involved (1) model representation of the specimen as the sum of homogeneous, practically noninteracting volumes, (2) a specific form of the distribution function for these volumes over the Curie temperatures, and (3) the fact that the numerical coefficients in the analytic expression for the singularity are independent of the deviations in the composition and structure of the homogeneous volumes from the mean. Assumptions of the second kind require that the specific-heat singularity in the ideal case be symmetric and nearly logarithmic, and that the Curie point in the homogeneous nonideal specimen (or in a homogeneous volume) has the usual physical significance.

One would hope that the validity of the relations and estimates given above, confirmed by the analysis of our data and data taken from[1] and, in particular, the agreement between numerical values of the main parameters describing the specific-heat singularity obtained in different ways, is an indication that the above assumptions are correct.

[1] A. V. Voronel', S. R. Garber, and V. M. Mamnitskiĭ, Zh. Eksp. Teor. Fiz. 55, 2017 (1968) [Sov. Phys.-JETP 28, 1065 (1969)].

[2] M. A. Mikulinskiĭ, Zh. Eksp. Teor. Fiz. 55, 2376 (1968) [Sov. Phys.-JETP 28, 1261 (1969)].

[3] A. V. Voronel', Doctoral Dissertation, FTINT, Khar'kov, 1967.

[4] B. Ya. Sukharevskiĭ, A. V. Alapina, and Yu. A. Dushechkin, Zh. Eksp. Teor. Fiz. 54, 1675 (1968) [Sov. Phys.-JETP 27, 897 (1968)].

[5] B. Ya. Sukharevskiĭ, B. G. Alapin, and E. I. Aksel'rod, Dokl. Akad. Nauk SSSR 171, 359 (1966).

[6] J. W. Vervey and P. W. Haayman, Physica 8, 979 (1941).

[7] A. V. Alapina, Yu. A. Dushechkin, V. A. Kucheryavyĭ, and B. Ya. Sukharevdkiĭ, Fizika kondensirovannogo sostoyaniya (Physics of the Condensed State), Collection FTINT AN UkrSSR, Khar'kov, 1969.

[8] S. C. Abrahams and B. A. Calhoun, Acta Cryst. 8, 257 (1955).

[9] T. Jamamoto, O. Tanimoto, J. Jasuda, and K. Okada, Critical Phenomena. Proc. of a Conf., Washington, 1965, NBS, 1966, p. 86.

[10] L. Shvarts, Matematicheskie metody dlya fizicheskikh nauk (Mathematical Methods for Physical Sciences), Izd. Mir, 1965.

Translated by S. Chomet
183