SPECIFIC HEAT OF Gd NEAR THE CURIE POINT

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Submitted to JETP editor March 10, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 49, 429-432 (August, 1965)

The specific heat of two Gd samples [$\rho(300°K)/\rho(4.2°K) = 12$ and 27] was measured near the Curie point. The problem of the influence of impurities on the singularity of the thermodynamic potential in a transition of the second kind is discussed and it is shown that the presence of such a singularity is masked by the imperfection of the samples. The incorrectness of the determination of the Curie point from the maxima of "nonmagnetic" properties is mentioned and the discrepancies between the published values of the Curie point, determined by using various properties, are accounted for.

Buckingham, Fairband and Kellers (cf. [1]) discovered a logarithmic singularity of C_p at the λ-point of He. The generality of this result was limited by the fact that $C_p(T)$ was measured near a critical transition point of the second kind (in accordance with the terminology used in the book of Landau and Lifshitz [2]). Therefore, it seemed interesting to investigate the singularities of the thermodynamic quantities at a normal transition point of the second kind, for example, at a ferromagnetic transition point.

We chose to investigate Gd, an element with its Curie point at 290°K, i.e., in the range of temperatures where the method of Strelkov et al.[3] can be applied. We had two samples at our disposal, for which the resistivity ratios $\rho(300°K)/\rho(4.2°K)$ were, respectively, 12 and 27 and whose weights were ≈ 70 and ≈ 1.2 g. We shall denote them by Gd_{12} and Gd_{27}. The purity of the samples (in at.%) was $\approx 98.5-99.0$ for Gd_{12} and $\approx 99.3-99.7$ for Gd_{27}. Sample Gd_{27} was annealed at 900°C.

The dependence $C_p(T)$ for Gd was determined very accurately (to within 0.1%) by Griffel et al.,[4] but their data were not sufficiently detailed near the Curie point. The sample used by Griffel et al. will be denoted by Gd_x. Its purity was 99.4–99.5 at.%.

The measurements on the Gd_{12} sample were carried out using the standard calorimetric apparatus [3] with an accuracy of 0.5%. Some idea of the construction and dimensions of the calorimeter used for Gd_{27} can be obtained from Fig. 1. The sample (8) is wrapped in cigarette paper (4), impregnated with BF-2, on which a bifilar thermometer-heater (6), made of platinum wire 0.05 mm in diameter, is wound tightly. A copper wire 5 (PEL, 0.05 mm diameter) prevents the short-circuiting of neighboring turns of the thermometer-heater. The thermometer leads are in the form of miniature (≈ 0.1 g) beads with platinum loops (1, 2). The sample is centered in a copper jacket 7 (wall thickness ≈ 0.1 mm) by means of two paper washers 3. The calorimeter is filled with the heat-carrier gas (He) and hermetically sealed.

The accuracy of the calibration and the stability of the thermometer were better than 0.01 deg. The precision with which the adiabatic conditions

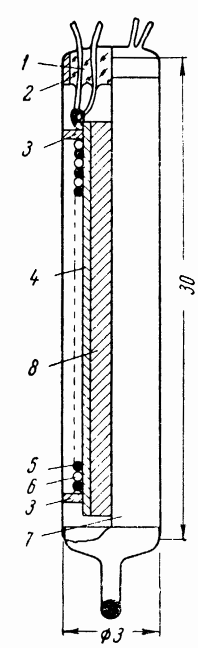

FIG. 1. Construction of the calorimeter used for sample Gd_{27}.

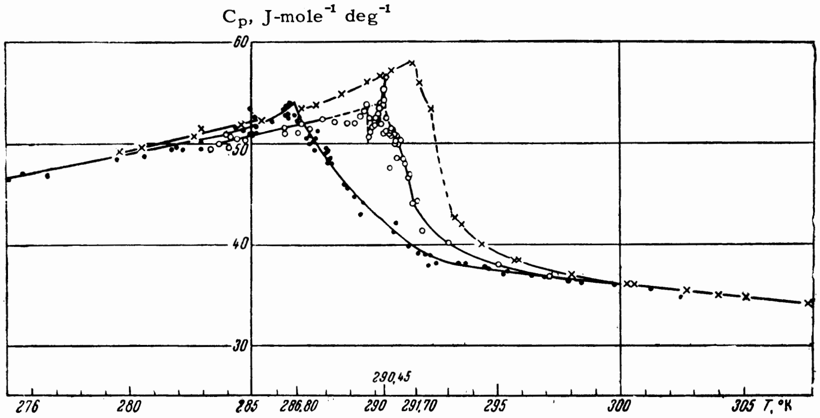

FIG. 2. Dependence $C_p(T)$ for samples ● – Gd_{12}, ○ – Gd_{27}, × – Gd_x.

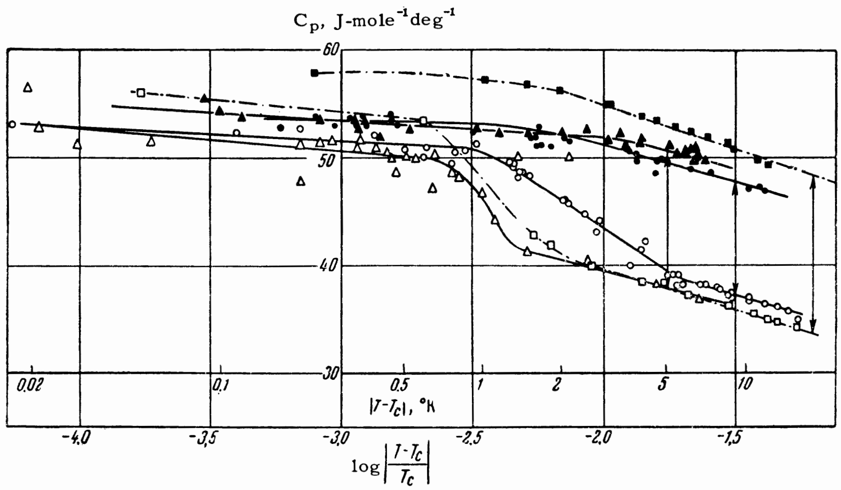

FIG. 3. Dependence of C_p on $\log|(T - T_C)/T_C|$ for samples, ○, ● – Gd_{12}, △, ▲ – Gd_{27}, □, ■ – Gd_x; open symbols represent $T > T_C$, black samples represent $T < T_C$.

were maintained had to be improved to (2–3) $\times 10^{-4}$ deg using a semiautomatic circuit, based on a F-16 photomultiplier specially developed by V. M. Mamnitskiĭ. The accuracy of the results obtained was ≈ 1–1.5% for steps ≥ 0.2 deg in the calorimetric measurements.

The results of our measurements are shown in Fig. 2. In Fig. 3, the same data are plotted on a semilogarithmic scale.[1)] For convenience, Fig. 3 includes the approximate $|T - T_C|$ scale. The temperature of the maximum of the $C_p(T)$ curve was arbitrarily assumed to be T_C (Fig. 2).

We can easily see that our curves differ considerably from the results of Buckingham and Fairbank [1] and are closer to the curves reported by Anderson [5] for C_p of the antiferromagnet MnS and by Chashkin et al.[6] for C_V at the critical point of air. There is no tendency for the specific heat to rise to infinity and the specific heat maximum occurs at a temperature different from that of the "discontinuity." (The "discontinuity" is given in quotes because it was strongly broadened. In fact, what we observed was not a discontinuity but a fall in the specific heat, which was faster than that at other temperatures). Thus, from the nature of the data obtained, we may assume that we are dealing with a logarithmic singularity deformed due to its being very close to a transition point. Obviously, the broadening of the singularity, the reduction and broadening of the discontinuity, and the difference between the temperatures of the maximum and the discontinuity can be treated as the consequence of imperfections in the ferromagnetic crystal. This point of view is reasonable because it is evident from the $C_p(T)$ curves for different $\rho(300°K)/\rho(4.2°K)$ that the purer sample Gd_{27} has a more definite (sharper) discontinuity. The broadened width of the discontinuity is ≈ 4 deg for Gd_{12} and ≈ 0.7 deg for Gd_{27}. Consequently, the slope of the "discontinuity" is ≈ 3 J-mole^{-1} deg^{-2} for Gd_{12} and ≈ 13 J-mole^{-1} deg^{-2} for Gd_{27}.

The separation between the maximum and the "discontinuity" for Gd_{27} ($\approx$1.3 deg) is much

[1)]A weak anomaly was observed in the curve for Gd_{27} in the temperature range 289.6–290.4°K. This anomaly had no connection with the problems discussed in the present paper and, therefore, we did not plot the points related to it on the semilogarithmic scale of Fig. 3.

smaller than that for Gd_{12} (≈ 5 deg); a similar effect has been observed also for C_V of nitrogen containing different amounts of impurities.[6] We can expect that in an ideal magnetic sublattice this separation would be zero, the "discontinuity" would be sharp (vertical), C_p would tend to infinity, and T_C would become a sharp boundary representing the appearance (disappearance) of the ordering.

Obviously, in the first approximation, the degree of deformation of the specific heat singularity near the Curie point is governed by the total number of departures from the long-range order. However, it is more likely that different imperfections make different contributions to the distortions of the various elements of the transition: T_C, the "discontinuity," and the maximum.[2)] This problem may be solved completely only by determining the quantitative relationships governing the influence of various imperfections on the deformation of the elements of the specific heat curve. The deformation of the logarithmic singularity in nonideal samples may be represented qualitatively, using geometrical representations, as follows. Let us use d to denote the degree of departure from the long-range order. We shall consider the surface $C_p(T, d)$. When this surface is cut by the plane $d = 0$, we obtain a curve in which a symmetrical logarithmic singularity is superimposed on a vertical discontinuity at T_C. At low values of $d \neq 0$, we obtain curves with a broadened discontinuity and a finite maximum, which is a trace of the plane $d = \text{const}$ on the "cone" of the singularity. At high values of d, the maximum disappears, and the discontinuity becomes a gently sloping line and decreases strongly in amplitude. As $d \to \infty$ (for example, in a paramagnet), the $C_p(T, d)$ surface becomes a horizontal plane. The transition temperature in an impure sample loses the meaning of a sharp boundary. Obviously, it is basically wrong to identify the transition temperature with the temperature of the maximum (peak), which is a trace of the singularity. The ordering disappears at the end of the "discontinuity." This could explain the "discrepancy" between the values of T_c determined from the magnetic measurements, where the transition temperature is identified with the temperature at which the ordering disappears, and the measurements of the so-called "nonmagnetic" properties (such as C_p, α, $\rho^{-1}d\rho/dT$, etc.), where the temperature of the maximum is regarded as the Curie temperature.

It is known that in less imperfect samples this discrepancy is less. For example, Belov and Paches[7] found that in a Ni sample containing Si as an impurity, the discrepancy between the values of T_C, determined from different properties, decreased from 5.3 to 3.3 deg C after annealing. Figure 2 shows clearly that the temperatures of the ends of the "discontinuities" for all three Gd samples differ by not more than 1.5 deg (the experimental error is of the same order), while the clearly defined temperatures of the maxima of Gd_{12} and Gd_x differ by ≈ 5 deg. Thus, we can see that, of the elements of the transition, the singularity and the discontinuity are the most sensitive to departures from the long-range order.

We take this opportunity to thank K. P. Belov, A. V. Ped'ko, and R. Z. Levitin for kindly supplying sample Gd_{27} and for their interest in this work. We are also very grateful to G. V. Abramov and R. S. Aristov for their help with the time-consuming measurements, and to V. A. Konoplev for his advice and help in the construction of the thermometer-heater used for the Gd_{27} sample.

Note added in proof (July 6, 1965). After submitting this paper for publication, we measured the specific heat of nitrogen containing $\approx 3.5\%$ oxygen. The behavior shown in Fig. 2 was confirmed. The specific heat maximum corresponded to $T'_c = 126.95°K$, and the discontinuity occurred at $T_d = 127.09°K$.

2)Sample Gd_x has the greatest "discontinuity" and the highest temperature of the peak. However, the sharpness of the "discontinuity" and the distance between the "peak" and the "discontinuity" were no better than for Gd_{27}.

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Translated by A. Tybulewicz
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