DETERMINATION OF THE CURIE TEMPERATURE OF A REAL SPECIMEN

A. V. VORONEL', S. R. GARBER, and L. D. PERETSMAN

Institute of Physico-technical and Radiotechnical Measurements

Submitted February 5, 1969

Zh. Eksp. Teor. Fiz. 57, 92–99 (July, 1969)

The heat capacity, effective permeability, and loss resistance were measured on three gadolinium specimens near the Curie point. It was observed that the maxima of these three quantities with respect to temperature do not coincide. It was found that the temperature of maximum permeability is closer to the Curie point than the temperature of maximum heat capacity. It is suggested that the most accurate information about the Curie temperature of an ideal specimen can be obtained by measurement of the loss resistance. The dependence of the permeability and the losses on temperature was found to have a hysteretic character, and the position of the maxima of these quantities was found to depend on frequency.

IT was shown earlier[1] that the problem of the form of the singularities of thermodynamic quantities at second-order phase transition points, for solid materials, cannot be solved without investigation of the factors that distort these singularities in real specimens. Attempts to interpret the results of experiments on the basis of a theoretical calculation of the effect of these factors are dependent on very strong assumptions about the character of the desired singularity. Thus the calculation of Belov and Paches,[2] carried out within the framework of Landau's theory,[3] is based on the assumption that the anomalies at the Curie point of a homogeneous alloy have the same character as those at the Curie point of a pure material. We note that the results of experimental researches[4,5] compel one to have doubts about this. In the calculation of Yamamoto et al,[6] just as in [2], the assumption is very essential that each homogeneous subsystem in a real specimen differs from the others only in its transition temperature. For the homogeneous system itself, there is postulated the existence of a symmetrical logarithmic singularity. Comparison with experiment has shown that a diffuse specific-heat anomaly almost always has a logarithmic section in a region that is narrow and, above all, far from the transition: $10^{-3} \lesssim (T - T_C)/T_C \lesssim 5 \times 10^{-2}$, where T_C is the temperature with respect to which the logarithmic section of the peak of the specific heat C_p is symmetric.

Unfortunately, because of the absence of criteria that would exclude arbitrariness in the choice of T_C, this fact does not mean that in an ideal material the singularity is also symmetric and logarithmic. It was shown in [1] that, depending on the choice of T_C, the same data could be used to support the use either of a symmetric or of an asymmetric singularity. Reese,[7] by choosing T_C appropriately, represented the specific-heat singularity (in KDP) both by power and by logarithmic functions.

Thus it seems to us necessary to find objective criteria for the determination of T_C in a real specimen. For this purpose, measurements were undertaken of the specific heat, magnetic permeability, and loss resistance near the Curie point for the same specimens of gadolinium in the same apparatus. Three specimens were investigated. Since the smearing-out factors obviously act differently on the anomalies of the different quantities, we hoped to obtain, as a result of such an experiment, an idea of just which property was least sensitive to distortions and gave a value of the temperature of the anomaly approximating most closely the assumed Curie temperature.

For interpretation of the results, we used the analogy between the Curie point and the liquid-vapor critical point, in the same way as in [1].

1. THE EXPERIMENT

The Gd specimens, as in [1], were characterized by the ratio of the resistance at room temperature ρ (300°K) to the resistance at helium temperature ρ (4.2°K): $k = \rho(300)/\rho(4.2)$.

The first specimen was a rod of irregular shape, of length ~40 mm and of mean diameter ~10 mm, with an opening of diameter ~1.5 mm for a platinum resistance thermometer. For this specimen, $k \approx 18$. The other two specimens had shapes reminiscent of a toroid, with internal diameter ~7 to 8 mm and external ~18 to 20 mm. These specimens were taken from an ingot in which the value of k varied throughout the volume of the ingot and ranged from 10 to 16. We shall designate our specimens as, respectively, Gd_{18}, Gd^1_{10}, and Gd^2_{10}.

The measurements of heat capacity were made in an adiabatic calorimeter.[8] To measure the magnetic permeability of the specimen Gd_{18}, a test coil was wound with copper conductor of diameter 1 mm in eight layers on an ebonite form (~250 turns). On the toroidal specimens, 400 turns of silk-insulated copper wire, of diameter 0.06 mm, were wound directly. For better thermal contact with the thermometer, both toroidal specimens were immersed in a vessel containing apiezon oil VM-1.

Measurement of the permeability of the specimens reduced to measurement of the change of inductance of the coils, of which the specimens were cores. Here what interested us was not the absolute value of the permeability μ, but only the location of the anomalies of this value, which obviously must coincide with the location of the anomalies of the measured inductance L.

The measurements of inductance and loss resistance

were made by means of a U592M apparatus for measurement of inductance and capacitance, with use of a GZ-33 generator and an F-510 null indicator, at frequencies from 30 to 5000 Hz. The output voltage of the generator (and thereby the amplitude of the alternating magnetic field acting on the specimens) was before each measurement chosen so small that the value of the inductance was independent of it. This amplitude was of the order of the earth's field, and this determined the limit of the field in which we worked. All measurements were made in the earth's magnetic field.

The inductance was measured first with gradual increase of the specimen temperature, and then with cooling. On specimen Gd_{18}, the measurements near the Curie temperature were made under operating conditions of continuous heating (and cooling) at the rate ~0.2 to 0.3 deg/hour. The inductance of the other two specimens was measured pointwise under adiabatic conditions, with a temperature rate of 0.001 deg/hour at each point. The loss resistance was measured simultaneously with the inductance and corresponded to the absorption of the energy of the electromagnetic field at the given frequency (the imaginary part of the permeability).

2. RESULTS OF THE MEASUREMENTS

Figure 1 shows the results of the measurements of heat capacity for all three specimens. The specimen Gd_{18} was measured most carefully, and for it the specific-heat curve is given. For the other two specimens, the measurements were made only to clarify the location of the maximum, and for them the values of the total heat capacity are given, without allowance for the heat capacity of the calorimeter.

Figures 2 and 3 illustrate the dependence, typical for all three specimens, of the inductance L and the loss resistance R on temperature for frequencies 500 and 5000 Hz. What interests us is the position of the maxima of the static values, and therefore we were obliged to study the dependence of the results of the measurements on frequency. Figure 4 shows a plot of the dependence of the position of the temperature T_m of the maxima of the permeability and of the loss resistance on the frequency of the measuring field. From 1000 Hz down, the position of the maximum is independent of frequency within the limits of accuracy of the experiment. This permitted us to determine the temperatures T_m of the maximum, for the permeability and the loss resistance, from curves obtained by measurements at frequency 500 or 1000 Hz, on which sufficient sensitivity was still retained.

The table shows values of the temperatures for maxima of all three quantities (C, L, and R) for all the specimens.

3. DISCUSSION OF THE RESULTS

1. It is evident from the table that the positions of the maxima on the heat-capacity and permeability curves do not coincide, and that for each specimen the maximum of the heat capacity lies at the lower temperature. It is obvious that the cause of this is imperfection of the specimens (inhomogeneity, impurities, etc.). In [9] it was shown experimentally how the curve of true heat capacity c_V near a liquid-vapor critical point is influenced by

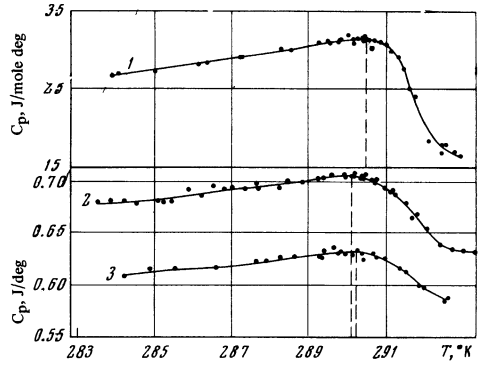

FIG. 1. Dependence of the heat capacity of three gadolinium specimens on temperature: curve 1, Gd_{18}; 2, $Gd_{10}{}^1$; 3, $Gd_{10}{}^2$.

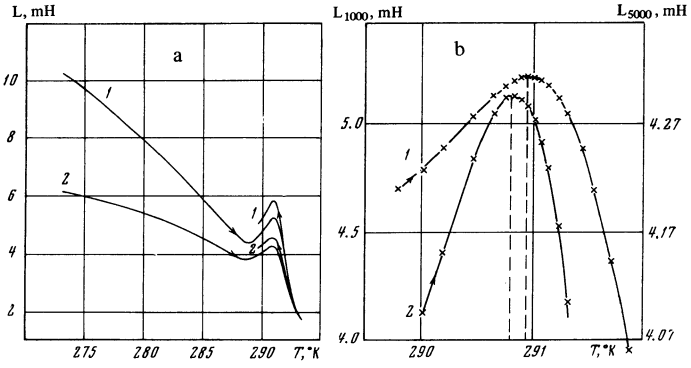

FIG. 2. a, Temperature dependence of the inductance L of a coil with core of gadolinium $Gd_{10}{}^1$ for frequencies 500 Hz (curve 1) and 5000 Hz (curve 2). The arrow shows the direction of temperature change. b, The same dependence near the maximum, for frequencies 1000 Hz (curve 1) and 5000 Hz (curve 2).

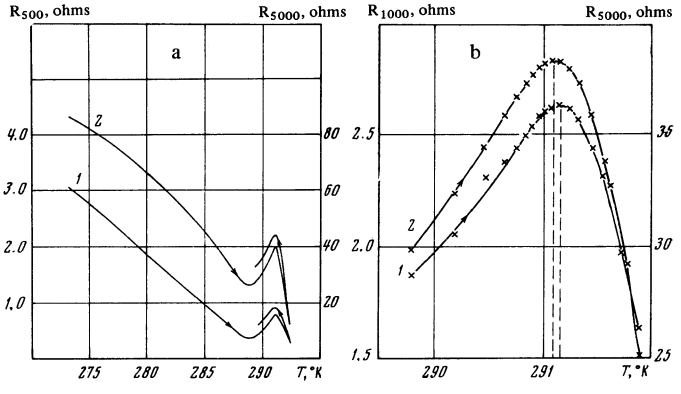

FIG. 3. a, Temperature dependence of the loss resistance R of a coil with core of gadolinium $Gd_{10}{}^1$ for frequencies 500 Hz (curve 1) and 5000 Hz (curve 2). The arrow shows the direction of temperature change. b, The same dependence near the maximum, for frequencies 1000 Hz (curve 1) and 5000 Hz (curve 2).

an inhomogeneity of the state of the specimen, when the inhomogeneity is described by the law

$$(\rho - \rho_c)^n \sim h. \qquad (1)$$

Here ρ is the density of the material; h is the height above the mean of the liquid column, where $\rho = \rho_c$;

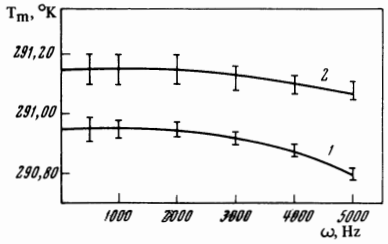

FIG. 4. Dependence of the temperatures of the maxima on frequency (specimen $Gd_{10}{}^{1}$). 1, for the curves L(T); 2, for the curves R(T).

Values of the temperatures for maxima of the curves $C_p(T)$, L(T), and R(T) for three gadolinium specimens

	Gd^1_{10}	Gd^2_{10}	Gd_{18}
$T_{m,C}$, °K	290.15±0.15	290.25±0.15	290.50±0.15
$T_{m,L}$, °K	290.95±0.05	291.25±0.05	291.35±0.10
$T_{m,R}$, °K	291.15±0.05	291.45±0.15	291.45±0.10

n = 3. (Thus is brought about a hydrostatic effect, the influence of the force of gravity on the density of the liquid in the critical state.) A calculation of Giterman et al.[10] showed that such results of [9] agreed with the assumption of a logarithmic dependence of the true heat capacity, $c \sim \ln(t + \beta v^2 + \dots)$, near the critical point (here $v = (V - V_c)/V_c$ is dimensionless volume). The measured heat capacity of an inhomogeneous system is obtained from the true by integration,[1)]

$$C_{\text{meas}} \sim \int_{-h}^{h} \rho(h) c dh. \qquad (2)$$

It is obvious that the more pronounced the inhomogeneity is—that is, the larger the exponent n is in formula (1)—, the more smoothed out the maximum of the heat capacity will appear, the further it will be shifted down in temperature, and the less isolated the temperature T_c will be on the curve of the function $C_{\text{meas}}(T)$.

Thus it was shown in [10] that for n = 3, the heat-capacity curve goes through T_c without any singularity, and the maximum is at a temperature T_m appreciably smaller than T_c; $T_m < T_c$ already for n = 1. In analogy to the expression (2), one can write for the total compressibility $V^{-1}(\partial V/\partial p)$ of an inhomogeneous system an integral expression, which describes the form of the dependence of the measured quantity on temperature. But in contrast to the heat capacity, whose singular part is expressed by the comparatively slowly increasing function $c \sim \ln(t + \beta v^2 + \dots)$, the compressibility has a strong singularity at the critical point. In first approximation

$$(\partial V / \partial p)_T \sim (t + \gamma v^2)^{-1}. \qquad (3)$$

This leads to the result that only for $n \geq 3$ is the maximum of the compressibility noticeably shifted, altho at temperature T_c the derivative of this quantity with respect to temperature (for n = 3) is still infinite. Thus inhomogeneity of the state shows up less strongly on the strong singularity present in the compressibility than it does on the heat-capacity curve.

[1)]The reader can find a more exact calculation in [10].

In analogy to this, it is to be expected that the maxima of the susceptibility (the value of the derivative of the magnetic moment with respect to field intensity, $(\partial M/\partial H)_T$, analogous to the compressibility of a liquid) of ferromagnetic Gd should show up as narrower and closer to the position T_C of an ideal specimen than do the maxima of the heat capacity C_p. The experimental data (Figs. 1–3 and the table) support this deduction. The maxima of the inductance in all three specimens are located to the right of the maxima of C_p, and closer to the T_C of an ideal specimen (this quantity is apparently larger than 292°K). The presence of noticeable shift and smearing out of the maxima of the magnetic permeability shows that the effective inhomogeneity of the magnetic moment in the specimens investigated is much more pronounced than that established at the critical point of a liquid because of the hydrostatic effect, and n in (1) may reach values of 5 or even 7.

2. In Figs. 2a and 3a, a fact that attracts attention is the presence of some hysteresis in the dependence of the permeability on temperature; it is especially noticeable near the Curie point. Actually the curve taken on cooling the specimen gives a higher value of the permeability. A similar phenomenon has already been observed in ferromagnets[11] (far from the Curie point) and in ferroelectrics[12] and is apparently due to obstacles to the movement of domain boundaries presented by impurities and other imperfections of the specimen. These imperfections appreciably lower the values of the permeability in a ferromagnetic specimen. But when the specimen approaches the Curie temperature from the side of the paramagnetic phase, the domains are formed initially in areas free from disturbances and make the largest possible contribution to the value of the permeability.

Thus from the experiment the conclusion follows that near the Curie point, along with the magnetization inside a domain, a large role is possibly played also by the process of movement of domain boundaries.

3. Since gadolinium possesses a quite large electrical conductivity, one can attempt to explain the change of the measured inductance and loss resistance in our experiment with frequency as due to the occurrence of eddy currents in the specimen. For sufficiently high frequencies, one can write approximately[13]

$$L \sim \sqrt{\mu / \omega\sigma}, \quad R \sim \sqrt{\mu\omega / \sigma}, \qquad (4)$$

where μ is the permeability, σ is the electrical conductivity, and ω is the frequency. It is seen from these formulas that on increase of frequency the induction drops, whereas the losses increase. We observe precisely this picture by experiment.

From (4) it also follows that if the $\mu(T)$ curve has a maximum, then a maximum should be observed both on the L(T) curve and on the R(T) curve, at the same temperature, independently of frequency (see, for example, [16]), if σ may with sufficient accuracy be considered a monotonic function of temperature. Results of measurements of electrical resistivity on polycrystalline gadolinium[14] safely support this assumption. But as can be seen from Figs. 2b, 3b, and 4, not only the value of the inductance and losses but also the position of their maxima depends on frequency. Furthermore, the maximum of the losses at any frequency is located at a higher

temperature than the maximum of the permeability. Consequently, the presence of eddy currents alone is incapable of explaining completely the character of the dependence of the inductance and losses of the coil on temperature and frequency. The presence of a loss maximum on the curve of temperature dependence obviously suggests the existence, at each temperature, of some characteristic frequency ω_0 for a given specimen, or of a characteristic time $\tau \sim 1/\omega_0$ (provisionally, it may be called a relaxation time), which increases with rise of temperature.

From what has been said in the previous subsection, it may be assumed that near the Curie temperature an important role is played by processes of domain boundary movement; we therefore have the right to expect large relaxation times of order $1/\omega$, where ω is the frequency we are applying. Then for the permeability, only those results are to be considered thermodynamic which relate to zero frequency, or at any rate to frequency $\omega \ll \omega_0$.

The table contains just these, the values of T_m extrapolated to zero frequency. It is seen from Fig. 4 that the order of the corresponding relaxation times τ for our specimens is close to $\tau \sim 10^{-3}$ sec.

4. We now turn our attention to the difference in averaging between additive thermodynamic quantities and kinetic quantities having dispersion. In subsection 1 it was shown, for example, how the maximum of the heat capacity shifts in an inhomogeneous specimen near a critical point T_C. The time for establishment of equilibrium in the same specimen has a maximum, as before, at the same place as a homogeneous specimen.[9] A similar phenomenon was noticed also in [15]. This occurs because the relaxation times of different parts of the system are not added to each other, like the heat capacities or, let us say, the permeabilities. In an inhomogeneous system, the longest time constants τ appear as a characteristic of the system as a whole (in experiments of other nature, the shortest time constants may, on the contrary, stand out). Thus those parts of an inhomogeneous system that are closest to the state of an ideal specimen make the greatest contribution in the determination of kinetic quantities near the true critical temperature, since the relaxation time of an ideal specimen becomes infinite near this temperature. This argument leads us to the idea that the maximum of the losses in a specimen, which is of course related to its relaxation time, is located at a temperature that is closer to the true Curie point than are the maxima of the thermodynamic quantities considered above. Actually, as is seen from the table, the maxima of the losses in the specimens are located at temperatures still higher than are the maxima of the permeability, and consequently closer to T_C.

The insufficiently wide range of the frequencies used in our research prevents a complete description of the behavior of the maximum of the losses and of the inductance. From Fig. 4, however, it can be concluded that the characteristic frequency ω_0, which is connected with movement of domain walls (see subsection 2) or with some other macroscopic mechanism, approaches zero at some temperature $T_{m,R}$, and presumably in such a way that $(\partial\omega_0/\partial T)_{T=T_{m,R}} = \infty$. It makes sense to call this temperature the Curie point of the real specimen, since it corresponds to the largest relaxation time. It is seen from the table that this temperature $T_{m,R}$ is least sensitive to individuality of the specimen.

In conclusion, the authors must thank G. V. Abramova, L. A. Bogushko, and V. P. Voronov for help in the measurements.

[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] K. P. Belov, Magnitnye prevrashcheniya (Magnetic Transitions) Fizmatgiz, 1959 (translation: Consultants Bureau, 1961).

[3] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), "Nauka", 1964 (translation of earlier edition: Addison-Wesley, 1958).

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

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

[6] T. Yamamoto, O. Tanimoto, Y. Yasuda, and K. Okada, in Critical Phenomena: Proceedings of a Conference in Washington, NBS, 1965, p. 86.

[7] W. Reese and L. F. May, Phys. Rev. **162**, 510 (1967).

[8] A. V. Voronel', S. R. Garber, V. M. Mamnitskiĭ, and V. V. Shchekochikhina, Issledovaniya v oblasti teplovykh i temperaturnykh izmerenii (Investigations in the Field of Heat and Temperature Measurements). Trudy metrologicheskikh institutov SSSR (Transactions of the Metrological Institutes, USSR), No. 92 (152), Standartgiz, 1967, p. 66.

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

[10] A. V. Berestov, M. Sh. Giterman, and S. P. Malyshenko, Zh. Eksp. Teor. Fiz. **56**, 642 (1969) [Sov. Phys.-JETP **29**, 351 (1969)].

[11] N. A. Baranova and Ya. S. Shur, Dokl. Akad. Nauk SSSR **94**, 825 (1954).

[12] P. P. Craig, Phys. Lett. **20**, 140 (1966).

[13] R. M. Bozorth, Ferromagnetism (D. Van Nostrand and Company, Princeton, N. J., 1950).

[14] N. V. Volkenshteĭn and G. V. Fedorov, Izv. Akad. Nauk SSSR, ser. fiz., **25**, 1379 (1961) [Bull. Acad. Sci. USSR, Phys. Ser., **25**, 1391 (1961)].

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

[16] K. P. Belov and N. V. Shebaldin, ZhETF Pis. Red. **7**, 268 (1968) [JETP Lett. **7**, 208 (1968)].

Translated by W. F. Brown, Jr.
12