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The role of demagnetization factor in determining the 'true' value of the Curie temperature

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ABSTRACT

The Curie temperature, T_C, is the temperature above which a material loses its long-range ferromagnetic order. Considering the equation of state of a ferromagnet in the mean-field approximation it has been shown theoretically that the value of the demagnetization factor N has a significant influence on the perceived location of T_C on the temperature scale. A series of precise measurements of magnetization using two differently shaped single crystals of high-purity gadolinium was carried out to prove this result experimentally and develop a procedure leading to the 'true' value of T_C.

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1. Introduction

The Curie temperature, T_C, is an important parameter for any ferromagnetic material and its precise experimental determination is of considerable value to physics of magnetism. T_C is the temperature above which a material loses its long-range ferromagnetic order. In the absence of magnetic field at temperatures below the T_C the magnetic moments are completely or partially aligned within magnetic domains. As the temperature increases towards the T_C, the alignment (magnetization) within each domain decreases. Above T_C, the material is purely paramagnetic and there are no magnetic domains of aligned moments.

This definition of the Curie temperature is applicable to any magnetic material, which undergoes a ferromagnetic–paramagnetic (FM–PM) transition in the absence of magnetic field, but it does not specify how to determine the value of T_C. We begin with a common assumption that T_C is a unique property of every ferromagnetic material, which undergoes a second-order phase transition in a zero magnetic field, and that the observed T_C depends only on the material itself.

Owing to the presence of 'tails' of the spontaneous magnetization and to the influence of paraprocess, there may be considerable difference between the values of the Curie temperature determined by different methods, in particular for multiple component alloys [1]. The following techniques to determine T_C are relatively straightforward and well-known:

1) from the extremum of the temperature coefficient of the electrical resistance $\frac{1}{R_0}\frac{dR}{dT}$ [1];
2) from the maximum of the negative galvanic magnetic effect (caused by the paraprocess) $-(\Delta R/R)_n$ [1];
3) from the drop of the magnetization $M(T)$, or from the minimum of dM/dT [2];
4) from the vanishing of initial permeability [1];
5) from the isothermal heat capacity measurements $C(T)$ in zero and nonzero magnetic fields. Maximum of the specific heat is observed at the Curie temperature [3].

The fact is that even though the galvanic magnetic effects are measured in cases 1 and 2, the extremum values of these effects (which are actually used to determine the location of T_C) occur when spontaneous magnetization is still substantial. According to Belov [1] and Belov and Goryaga [4] and to our own experience, none of the techniques that employ spontaneous magnetization (1–3) may be considered reliable since all of them greatly depend on the existence of the so-called 'tails' of spontaneous magnetization. These tails arise because of the remnants of the spontaneous magnetization above T_C. According to thermodynamics these remnants should not exist above T_C but in reality they are always present. That is why the procedure of determining the spontaneous magnetization by linear extrapolation of the curves of the true magnetization to zero field cannot be used near the Curie temperature, since in this region the curves are nonlinear. This is

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especially noticeable in alloys when the difference between the Curie temperature determined using different methods increases with increasing of the concentration of the nonmagnetic element in an alloy. Thus the broader the magnetic transition spreads out, the larger is the difference in the values of T_C determined by different methods.

Because of the effects of paraprocess, which can be important even in weak fields, the determination of the Curie temperature from the temperature dependence of initial permeability is the least exact method. Near the Curie temperature, magnetic anisotropy and magnetostriction are weak, and therefore, displacements and rotations of spins are hindered even in weak magnetic fields. In strong fields magnetization of a ferromagnetic material near the Curie temperature develops due to true magnetization (paraprocess), which is strong in this case and almost completely determines the ferromagnetic behavior of the substance. Paraprocess is caused by developing preferred orientation of spin and orbital magnetic moments in magnetic field, which are disordered without the field due to thermal energy. Since the maximum of specific heat can be very broad, the determination of the Curie temperature may also be difficult using this property.

Attempts have been made to determine the Curie temperature from the temperature dependence of residual magnetization and the coercive force [5]. This method fails often because either of these properties of a ferromagnetic material may have finite values even above the Curie temperature where 'remnants' of the spontaneous magnetization still exist. These effects go to zero only when the 'remnants' of the spontaneous magnetization completely disappear.

More exact methods to determine T_C include the Mössbauer technique and neutron scattering [6,7]. In the first case, one can observe vanishing hyperfine magnetic nuclear field at the Curie temperature. In the second approach, the isothermal measurements of magnetic scattering facilitate observation of the collapse of the long-range magnetic order at T_C. These methods are not in common use to determine T_C due to complexity of experimental equipment and also due to relatively high cost of such investigations.

In the middle of 1950s Belov and Goryaga [4] method proposed a technique leading to accurate values of T_C from magnetization measurements. This method is still used today, and it is better known as the Arrott method [8], which was proposed a year later. Belov–Goryaga–Arrott method is the most reliable for calculating T_C, since it is the only method where magnetic data are used to support a fit based on the thermodynamic theory.

The Belov–Goryaga method uses Landau's expansion of the thermodynamic potential [9] Φ into a series of magnetization powers with appropriate coefficients

$$\Phi = \Phi_0 + \frac{1}{2}aM^2 + \frac{1}{4}bM^4 + \frac{1}{6}cM^6 + \ldots - HM \tag{1}$$

Landau's expansion has no physical meaning here; it is simply a technique to expand $M(H)$. At equilibrium $\partial\Phi/\partial M = 0$, and in terms of the so-called reduced magnetization, σ, and temperature, τ,

$$\sigma = \frac{M}{M_0}, \quad \tau = \frac{T}{T_C} \tag{2}$$

where M_0 is the saturation magnetization and T_C is the Curie temperature, Eq. (1) is transformed as follows:

$$H = a\sigma + b\sigma^3 + c\sigma^5 + \ldots \tag{3}$$

The coefficients on the right-hand side of Eq. (3), which are regarded as functions of reduced temperature, are expanded in the Taylor series about the Curie temperature, i.e. about $\tau = 1$, where explicit expression for a is [10]

$$a(\tau) = a(1) + a'(1)(\tau - 1) + \frac{1}{2}a''(1)(\tau - 1)^2 + \ldots \tag{4}$$

The coefficient a can be determined from isothermal field dependencies of magnetization and since $a = 0$ at T_C, this can be used to determine the Curie temperature.

2. Theoretical considerations

Consider the equation of state of a ferromagnet in the mean-field approximation [11]

$$y = B_J\left(\frac{3J}{J+1}\frac{T_C}{T}y + \frac{\mu H}{kT}\right) \tag{5}$$

Here $y = M/M_0$, where M is the magnetization and M_0 is the saturation magnetization, B_J is the Brillouin function [12], J is the total angular momentum quantum number, T is the temperature, k is the Boltzmann constant, μ is the magnetic moment (for Gd the 4f contribution to the magnetic moment is 7 μ_B), and H is the internal magnetic field; $H = H_{external} - NM$, where N is the demagnetization factor. The second term in Eq. (5) is much smaller than the first one since exchange field dominates the magnetostatic field in a ferromagnet. In the absence of external magnetic field, $H = -NM = -NM_0y$. Thus

$$y = B_J\left(\frac{3J}{J+1}\frac{T_C}{T}y - \frac{\mu NM_0}{kT}y\right) \tag{6}$$

This can be rewritten as an equation of state of a ferromagnet without the applied external field

$$y = B_J\left(\frac{3J}{J+1}\frac{T'_C}{T}y\right) \tag{7}$$

where T'_C is the observed Curie temperature, modified by the demagnetization factor as follows:

$$T'_C = T_C\left(1 - \frac{J+1}{3J}\frac{\mu NM_0}{kT_C}\right) \tag{8}$$

An estimate of the maximum shift of T_C for $N = 4\pi$ for some common ferromagnets is given in Table 1.

Thus, the value of the demagnetization factor N has a significant influence on the location of the measured T_C on the temperature scale. And demagnetization factor, in turn, greatly depends on the shape of the sample.

To justify the obtained theoretical result we repeated the calculation of the possible T_C shift as a function of the demagnetization factor based on the Landau theory of second-order phase transitions (i.e. without the Brillouin theory). Substituting the external field contribution into the thermodynamic potential in Eq. (1) by the demagnetization field contribution one can estimate the possible shift of the Curie temperature. For the sample of Gd in the shape of the flat parallelepiped (the plate) with the demagnetization factor 0.83 the estimated shift is 2.5 K, which agrees with that obtained using the Brilloiun theory.

Next, we discuss the measured magnetic properties of two differently shaped samples made from the same material in order to show experimentally that the measurements of the Curie

Table 1
Maximum shift of T_C for Ni, Fe, and Gd calculated using Eq. (8) and $N = 4\pi$.

Metal	M_0 (emu/cm^3)	J	μ (μ_B)	$T_C - T'_C$ (K)
Ni	510	1/2	0.6	0.3
Fe	1750	1	2.2	2
Gd	2120	7/2	7	5

temperature, T_C, are influenced by the shape of a ferromagnetic material. This work is not a study of critical behavior; the main goal is to establish how the Curie temperature, T_C, is dependent on the demagnetization factor, N.

3. Experimental technique

We chose Gd because it is one of the well-known examples of the magnetic materials with second-order phase transition, which was well studied in the past [13–18]. List of Curie temperatures determined for several different Gd samples can be found in Ref. [14].

Two single crystalline samples were made from high-purity Gd (99.98+at% purity with respect to all other elements in the Periodic Table). Since purity and related defects may significantly influence the character of the phase transition we believe that only high-purity single crystals are suitable for the aim of the present work. Since the samples were cut from the same grain of a single crystal of Gd produced using the strain anneal technique, it is extremely unlikely that any detectable difference of their properties may be related to chemical inhomogeneity of the original single crystalline grain, especially considering that this is an elemental material and not a multicomponent alloy.

Gadolinium was prepared by the Materials Preparation Center of the Ames Laboratory using the 'Ames method' [19–21], which starts with the highest purity rare earth-oxide (commercially available) treated with the anhydrous HF. The resulting rare earth-fluoride is then reduced with triple distilled calcium to produce pure metal. The rare earth metal is further purified by distillation or sublimation, and a single crystal is grown using the strain anneal technique.

Gadolinium single crystalline samples in the shape of an elongated parallelepiped (rectangular rod, $m=30.6$ mg) with the dimensions 0.65 mm × 0.56 mm × 11.62 mm and a flat parallelepiped (plate, $m=29.3$ mg) with the dimensions 4.43 mm × 3.10 mm × 0.30 mm were chosen for a series of detailed magnetic measurements to verify theoretical predictions regarding the observed T_C. The longest axis of the rod was parallel to the hexagonal c-crystallographic axis of Gd. For the plate, the shortest axis of the parallelepiped coincided with the hexagonal c-axis. It is worth mentioning that the plate is not a two-dimensional system; it is still a bulk material. Crystallographic directions were determined using the back reflection Laue technique. The combined accuracy of the alignment of the crystallographic axes with the direction of the magnetic field vector was of the order of $\pm 5°$.

The detailed dc magnetization data were measured isothermally as a function of magnetic field using the Quantum Design ac/dc susceptometer/magnetometer MPMS-XL7. The magnetic measurements were carried out in the range of magnetic fields varying from 0 to 60 kOe (the field step was 4 kOe) and in the temperature interval from 280 to 300.2 K (from 280 to 290 K the step was 0.5 K; from 290.2 to 296 − 0.2 K, and from 296.2 to 300.2 − 0.5 K), with the accuracy better than 1%. Demagnetization factors were calculated using two different approaches. The first one considers the samples as the general ellipsoids resulting in the values of demagnetization factors N of 0.01 and 0.87 for the rod and the plate, respectively. These values were obtained using Figs. 1–3 of Ref. [22], and then multiplied by 4π and the density of Gd to simplify the procedure according to which the demagnetization factor has been taken into account. Another, more realistic possibility is to treat the samples as rectangular prisms. The same numerical procedures as in the first approach with the values taken from the Table II of the Ref. [23] were carried out. In this case, the corresponding values are 0.023 and 0.83 for the rod and the plate, respectively (with an accuracy of about 10%). They also were multiplied by 4π and the density of Gd and the values used below are 2 and 82, respectively. Since the values of the demagnetization factors calculated from two different approaches are close to one another, and our samples are in the shape of parallelepipeds we worked with the values determined from rectangular prisms approach. The results for N values obtained using general ellipsoids approach are presented for comparison.

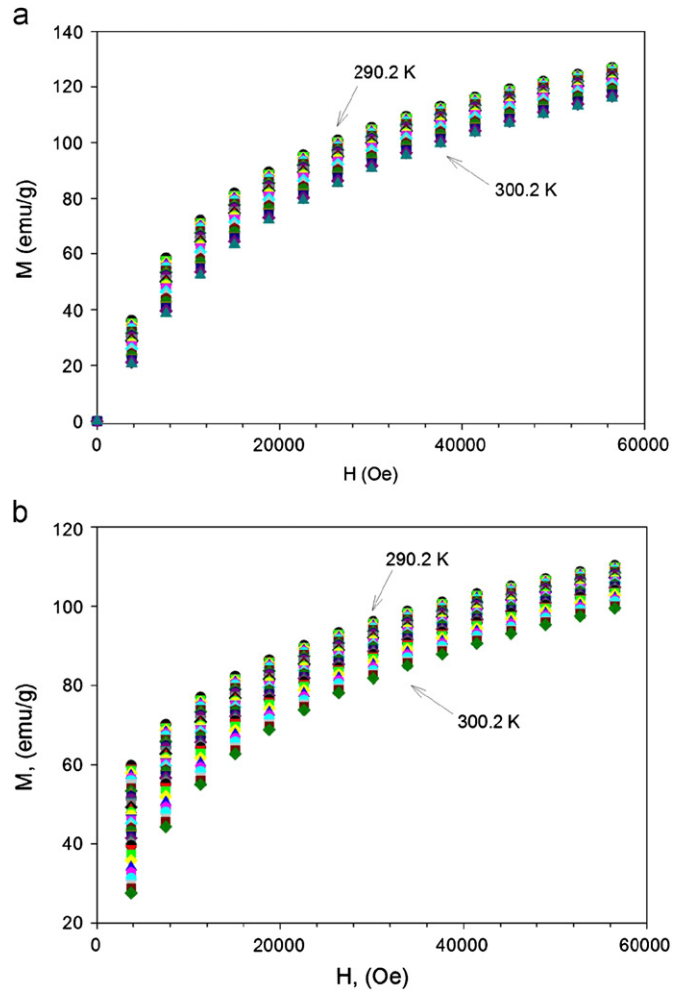

Fig. 1. Isothermal field dependencies of measured magnetization for the Gd sample in the shape of (a) flat parallelepiped (the plate) and (b) elongated parallelepiped (the rod) in the vicinity of the assumed T_C of Gd. Only the data between ~290 and ~300 K are shown for clarity, even though we used all of the data measured between 280 and 300 K for analysis.

A mathematical analysis (determination of the Curie temperature from magnetization curves) of the raw data with the demagnetization factor taken into account was performed using Belov–Goryaga [1,4] (Arrott [8,24]) method (also see the Introduction).

The following experimental procedure was used to determine the a values. First, $M(H)$ experimental data (Fig. 1a,b) were converted into a set of $H/M(M^2)$ curves. These experimental $H/M(M^2)$ curves (the so called Belov curves) are presented in Fig. 2a,b. Then every $H/M(M^2)$ curve in the vicinity of the assumed T_C was fitted linearly or using a second-order polynomial (in fields exceeding 2 T). From such a fit, a set of a values as the points where the fitted polynomial intersects the H/M axis (Fig. 3) was obtained. After that $a(T)$ plots were constructed. The point where $a(T)$ plot intersects the T axis is taken as the intrinsic 'true' T_C since a equals zero at the Curie temperature.

Correction for the demagnetization factor was done by shifting (which is possible since the demagnetization factors have been

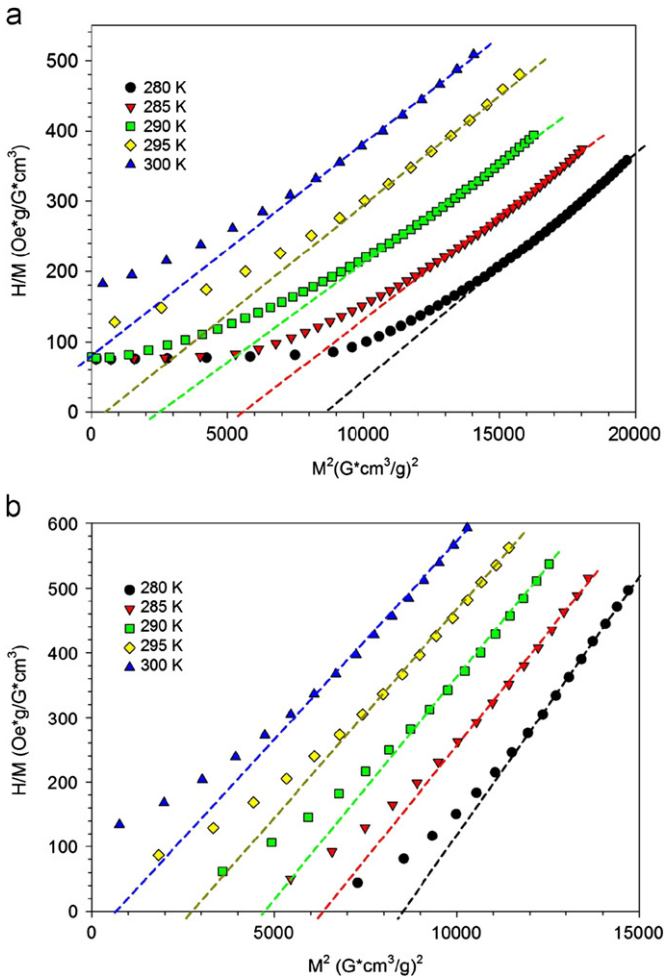

Fig. 2. Experimental Belov curves (H/M vs M^2 dependencies) without demagnetization correction for the Gd sample in the shape of (a) flat parallelepiped (the plate) and (b) elongated parallelepiped (the rod) in the vicinity of the assumed T_C of Gd.

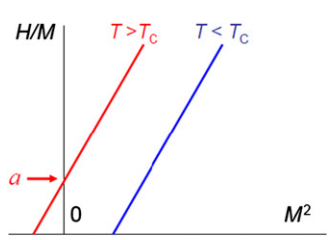

Fig. 3. Determination of the thermodynamic coefficient a in the Belov–Goryaga method (linear approximation of Belov curves).

already multiplied by 4π and the density of Gd) the $H/M(M^2)$ curves along the H/M axis by the value of the demagnetization factor N since

$$\frac{H}{M} = \frac{H_{external}}{M} - N \tag{9}$$

From the shifted curves, the a values were determined as described above.

It is worth noting that neither Belov–Goryaga's nor Arrott's original papers [4,8] consider the role of the demagnetization factor and crystallographic anisotropy of the material. The magnetocrystalline anisotropy of Gd is negligible, but in other materials its influence may be substantial.

The uncertainty of the Curie temperature has been estimated after considering the following three sources of errors in SQUID measurements: (1) sample mass error; (2) temperature error; and (3) magnetic moment measurement error. The latter is a combination of a field setting error and an actual measurement (fitting) error. Even though the sample mass has little effect on the observed T_C as long as its mass remains constant during the measurement, both samples were weighed with ± 0.1 mg accuracy. According to Quantum Design, temperature fluctuations inside the sample chamber are within 0.1 K. They also note, however, that the sample temperature is considered stable if the deviation is less than 0.5% from the setpoint. Hence, temperature errors may be as large as ~ 1.5 K around 300 K if a system does not reach thermal equilibrium, which is common if not enough time is allowed during changing temperature. In this work, long waiting periods for each temperature (very finely spaced, i.e. by 0.2 K in the immediate vicinity of T_C or 0.5 K away from T_C) have been implemented in order to approach a nearly ideal thermal equilibrium, and therefore, sample temperature errors were close to 0.1 K due to normal thermal fluctuations. The magnetic moment errors have little relevance on the observed value of T_C as long as they remain small and uniform throughout the measurements; in the SQUID the moment is measured with better than 1% accuracy. Considering all of the above, we believe that the 0.2 K (i.e. temperature separation during the measurements) is a reasonable estimate of the uncertainty with which the Curie temperatures have been determined in this work.

4. Results and discussion

Using the approach described above and $a(T)$ curves that are shown in Fig. 4, we determined the 'true' value of T_C for gadolinium as 290.6 ± 0.2 K for both the rod and the plate.

Fig. 5 also shows the $a(T)$ curves obtained using the ellipsoidal demagnetization factors. While the ellipsoid approach may not be as realistic as the parallelepiped one, and determined values of T_C are slightly different for the rod and the plate they remain close to the value of 290.6 K. Thus, one can conclude that taking demagnetization factor into account, i.e. eliminating the influence of the demagnetization field (in other words considering different samples at the same conditions), one can get the 'true' value of T_C for gadolinium.

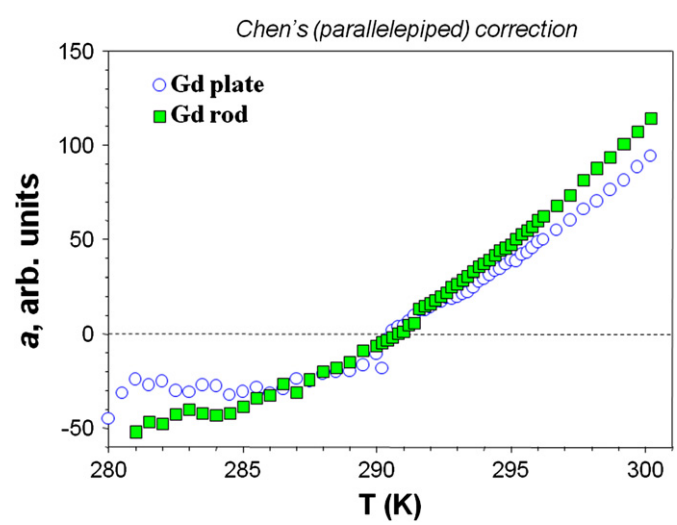

Fig. 4. Temperature dependencies of a for both the rod and the plate of Gd in the temperature interval 280.0–300.2 K with the demagnetization factor determined using the method of rectangular prisms.

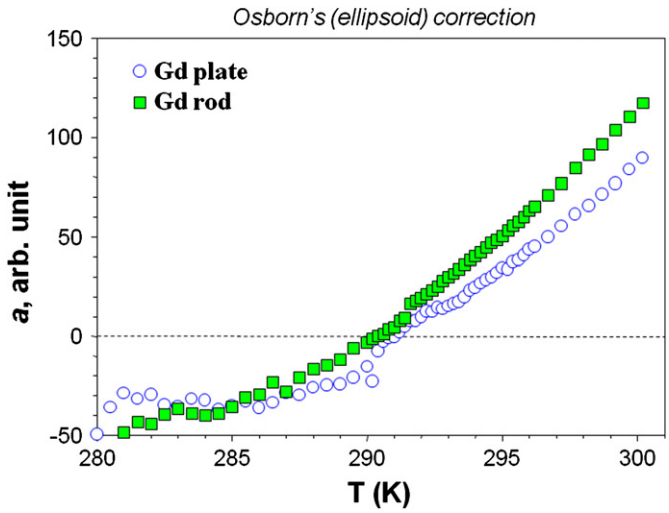

Fig. 5. Temperature dependencies of a for both the rod and the plate of Gd in the temperature interval 280.0–300.2 K with the demagnetization factor determined using the method of approximate ellipsoids.

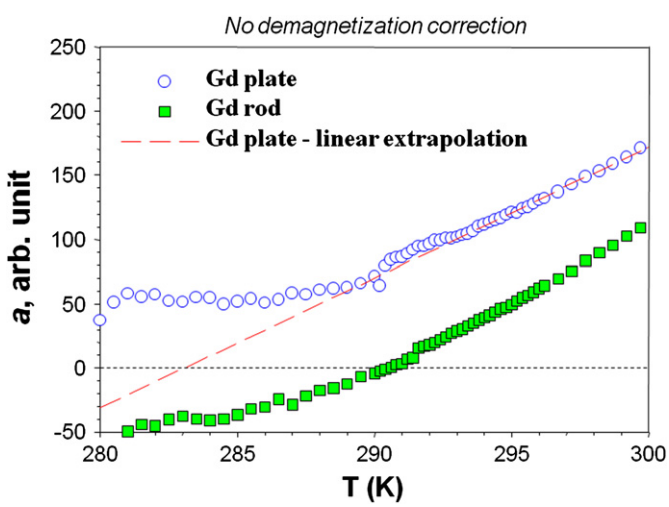

Fig. 6. Temperature dependencies of a for both the rod and the plate of Gd in the temperature interval 280.0–300.2 K without taking into account the demagnetization factor.

The influence of the demagnetization factor on T_C value is illustrated in Fig. 6. The observed shift of the perceived T_C for the plate, whose demagnetization factor is huge, is in good agreement with Eq. (8). Even though Belov and Arrott used linear fits to determine the temperature at which a becomes zero, the data for the plate indicate that the behavior is far from linear. Regardless of the poor fit, linear extrapolation of all data shown in Fig. 6 indicates that the perceived T_C of the plate may be as low as 276 K. Fig. 6 shows that the measured T_C of the plate determined using the data above the 'true' T_C is lower by more than 6 K compared to the measured T_C of the rod. The T_C value for the rod is slightly ($\sim$0.4 K) shifted towards lower temperature too.

In summary, we show that the measured T_C may not reflect the intrinsic magnetic property of a material as it depends on the shape of the measured sample, and we propose a general approach leading to the determination of the 'true' Curie temperature. The experimentally observed T_C is indeed affected by the demagnetization factor of the sample, i.e. is sample shape dependent. The T_C closest to the 'true' intrinsic value is approached when demagnetization factor of the sample approaches zero, i.e. $N \rightarrow 0$. Taking large values of the demagnetization factor N into account increases the error in the observed T_C due to increased errors in the measured values of the magnetization, and therefore, in the increased errors in the determination of a. Moreover, when the shape of the sample cannot be approximated by simple shapes (e.g. an ellipsoid, a sphere, or a rectangular prism) the approach described here can lead to an increased uncertainty in the determination of the T_C value.

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