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New acoustic detection technique for a magnetocaloric effect

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ABSTRACT

We present a new photoacoustic-like detection technique which allows for the rapid detection of small periodic temperature variations induced by small periodic adiabatic magnetic field variations imposed on a magnetic material. Results are presented for gadolinium near the Curie point. From the results for the periodic temperature variations of the sample information can be obtained about the magnetic equation of state.

INTRODUCTION

The first law of thermodynamics for reversible changes in magnetic systems can be written (Stanley, 1971, Kittel, 1967) in the following way :

$$dU = dQ - MdB = TdS - MdB, \tag{1}$$

where U is the internal energy, $dQ = TdS$ the heat change, with T the temperature and S the entropy. B is the applied magentic field and M the magnetization. In equation (1) it is assumed that any mechanical work can be neglected. On the basis of (1) the following Maxwell relation can be deduced :

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial M}{\partial T}\right)_B. \tag{2}$$

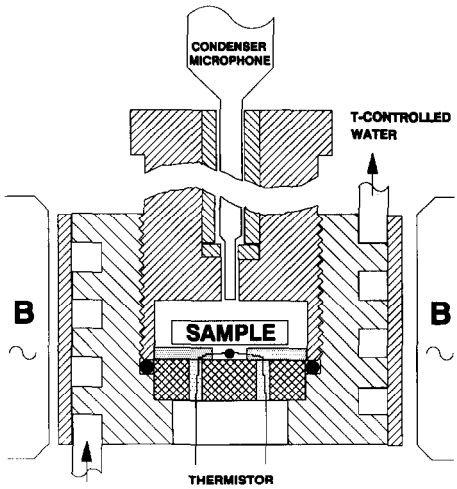


Fig. 1 Schematic diagram of the sample holder and sample

Introducing the specific heat capacity at constant applied field $C_B = T(\partial S/\partial T)_B$, one can rearrange equation (2) as follows :

$$\left(\frac{\partial T}{\partial B}\right)_S = - T\left(\frac{\partial M}{\partial T}\right)_B / T\left(\frac{\partial S}{\partial T}\right)_B = - \frac{T}{C_B}\left(\frac{\partial M}{\partial T}\right)_B . \qquad (3)$$

Since $(\partial M/\partial T)_B$ is normally negative an adiabatic field increase results in a temperature rise of the sample.

Standard measuring techniques for this magnetocaloric effect use rather large steplike or pulsed fields and temperature detection with a temperature sensor (e.g. a thermocouple or thermistor) in contact with the sample (Ponomarev, 1986). In the new photoacoustic-like detection technique which we present here, a temperature sensor in direct contact with the sample is not needed. Our method allows for the rapid detection of small periodic temperature variations induced by small periodic field variations. The use of periodic field variations offers the advantages of lock-in detection resulting in substanital increases in the signal-to-noise ratio. Furthermore it is also possible to measure as a function of the magnetic field by superimposing the periodic field variations on a static external field. It will be shown that our method can be used to obtain information on the magnetic equation of state. Results will be presented for gadolinium near the Curie point.

EXPERIMENTAL METHOD

In our experimental setup the sample is placed in a small gas tight cell (figure 1), and subjected to a periodically changing magnetic field of the following form :

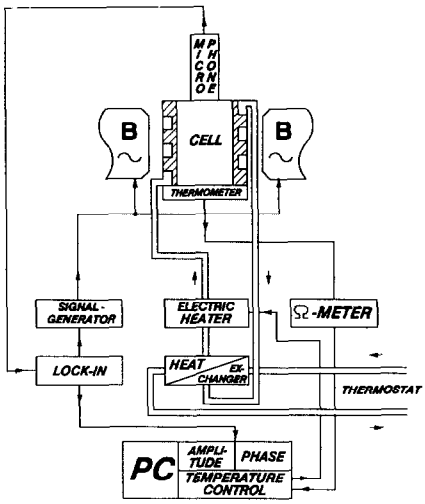


Fig. 2 Overview of the complete experimental setup

$$B = B_0 + B_1 \exp(i\omega t), \tag{4}$$

with B_0 a static field (from permanent magnets) and $B_1 (<< B_0)$ the amplitude of the harmonic field variation. The field modulation, parallel to B_0, is obtained with an alternating current flowing through coils (not shown) on two sides of the sample holder. The frequencies normally used are in the range between a few Hz and a few tens of Hz. The sample is mounted in very poor thermal contact with the walls of the sample holder and heat exchange mainly occurs with the gas (air) filling the cell. The harmonic modulation of the magnetic field (equation 4) gives rise to a corresponding temperature variation of the sample, resulting in an exponentially decaying thermal wave in the gas surrounding the sample. It can, however, be verified that the heat loss from the sample is very small over the time interval of the period of the field change. One can thus assume to work in a nearly adiabatic situation. The thermal wave in the gas causes periodic pressure changes in the cell which can be detected with a sensitive microphone in the wall of the sample holder.

The temperature is measured by means of a calibrated thermistor in contact with the wall inside the cell. Temperature control of the sample is achieved by means of a temperature controlled water flow through a helical cavity in the outer wall of the sample holder. The value of the static magnetic field B_0 and the amplitude B_1 are measured using a Hall probe (not shown in figure 1).

In figure 2 an overview of the whole experimental setup is given schematically. The microphone signal (at the modulation frequency) is detected by means of a lock-in detector connected to a personal computer (PC) for amplitude and phase (of the acoustical signal) data storage. The PC is also used to control the instruments for measuring and regulating the temperature of the cell.

In order to arrive at an expression for the acoustical signal generated by the harmonic field modulation given in equation (4), one can start with the magnetic work term $dW = M(B_0)dB$ in equation (1). One obtains then the following result for the power:

$$P(t) = dW/dt = M(B_0)dB/dt = i\omega B_1 M(B_0)\exp(i\omega t) = P_0\exp(i\omega t) \qquad (5)$$

If one now uses the Rosencwaig-Gersho (1976) theory from photoacoustics for an homogeneously heated sample one obtains :

$$\theta_0 = \frac{P_0}{i\omega\rho C_B} = \frac{B_1 M(B_0)}{\rho C_B}, \qquad (6)$$

for the amplitude θ_0 of the temperature variations at the surface of the sample (with density ρ). The amplitude R of the acoustical signal detected by the microphone is proportional to θ_0 and given by :

$$R = \frac{\gamma p_0 \mu_g \theta_0}{\sqrt{2}\, l_g T_0} f_{cm} = f_{syst}\theta_0, \qquad (7)$$

where f_{cm} depends on the microphone and cell characteristics and is ω and T dependent, p_0 and T_0 are the equilibrium pressure and temperature of the gas in de cell, $\gamma = C_p/C_v$ is the ratio of the specific heat capacity at constant pressure and volume of the gas, μ_g is the thermal diffusion length in the gas and l_g the distance from the sample surface to the wall of the sample holder. In principle one can calculate the proportionality factor f_{syst}, but in practice it is much more convenient to derive it from a calibration procedure.

EXPERIMENTAL RESULTS

We have carried out a series of measurements for gadolinium near the Curie point (T_c = 20.9 °C). The sample, with dimensions of 0.25 x 5 x 9 mm was cut from a polycrystalline Gd metal foil (0.25 mm) obtained from Johnson Matthey (England). The sample purity was stated to be better than 99.9%. Data have been obtined for the amplitude R of the microphone signal as a function of the temperature for a series of values for the static magnetic field B_0. For the amplitude B_1 of the harmonic field modulation a value of 1.1 mT was chosen. This B_1 value was still about 7 times smaller than our lowest B_0 value (8 mT).

The R values have been converted into θ_0 values by means of a calibration procedure allowing the determination of the system factor f_{syst} in equation (7) as a function of temperature. Since the sample is a conductor, resistive heating power P(t) can be supplied by applying an alternating current to the sample. For that purpose four thin copper leads have been connected to the edges of the sample. From the measurement of the current through and the voltage over the sample together with the corresponding amplitude R of the acoustical

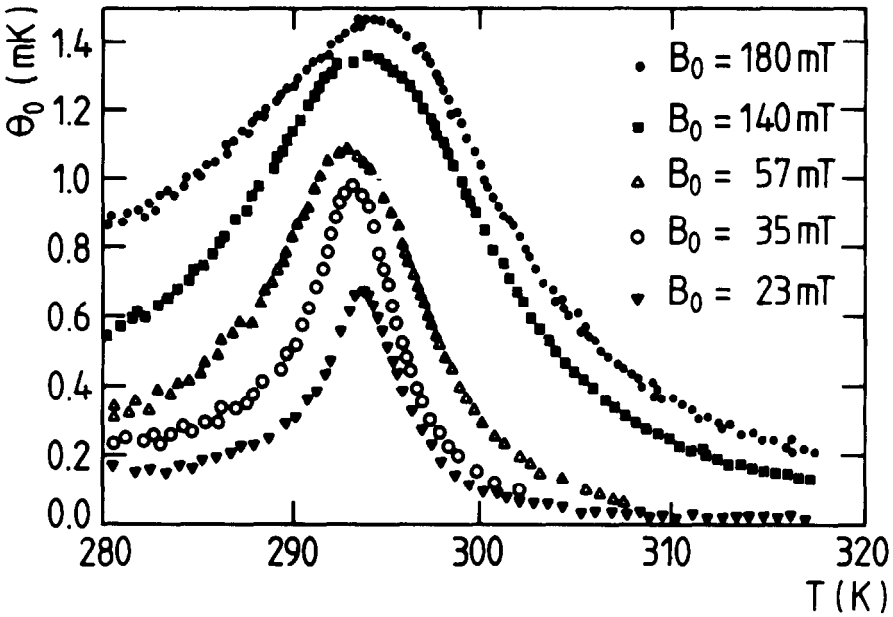


Fig. 3 Temperature dependence of the amplitude θ_0 of the adiabatic temperature variations in gadolinium near the Curie point ($T_c \approx 294$ K) induced by a harmonic field modulation with amplitude $B_1 = 1.1$ mT for different choices of the static field B_0.

signal it is possible to determine f_{syst}.

In figure 3 an overview of θ_0 values as a function of temperature is given for different choices of B_0. Data for several B_0-values are not given for display reasons. As can be seen from the figure our measuring technique allows us to detect very small temperature variations. The temperature resolution in the present configuration is of the order of 5μK. In figure 4 we give θ_0 values for several isotherms above and below T_c (estimated to be 20.9 °C for our sample) as a function of the static magnetic field B_0.

DISCUSSION

For a given choice of $B_1(<<B_0)$ it follows from equation (6) that θ_0 is proportional to the magnetization M (induced by the static field B_0), and inversely proportional to the product of the specific heat capacity C_B and the density ρ, which can be assumed to be independent opf the field and the temperature for not too large a temperature range. The magnetization and the specific heat capacity, however, are both functions of T and B_0. The data above T_c as well as below T_c are in qualitative agreement with equation (6), in the sense that $\theta_0(B_0)$ isotherms also start from zero and not from a value corresponsing with the spontaneous magnetization $M_s(T)$. We believe this to be a consequence of the polycrystalline nature of our sample, resulting in a

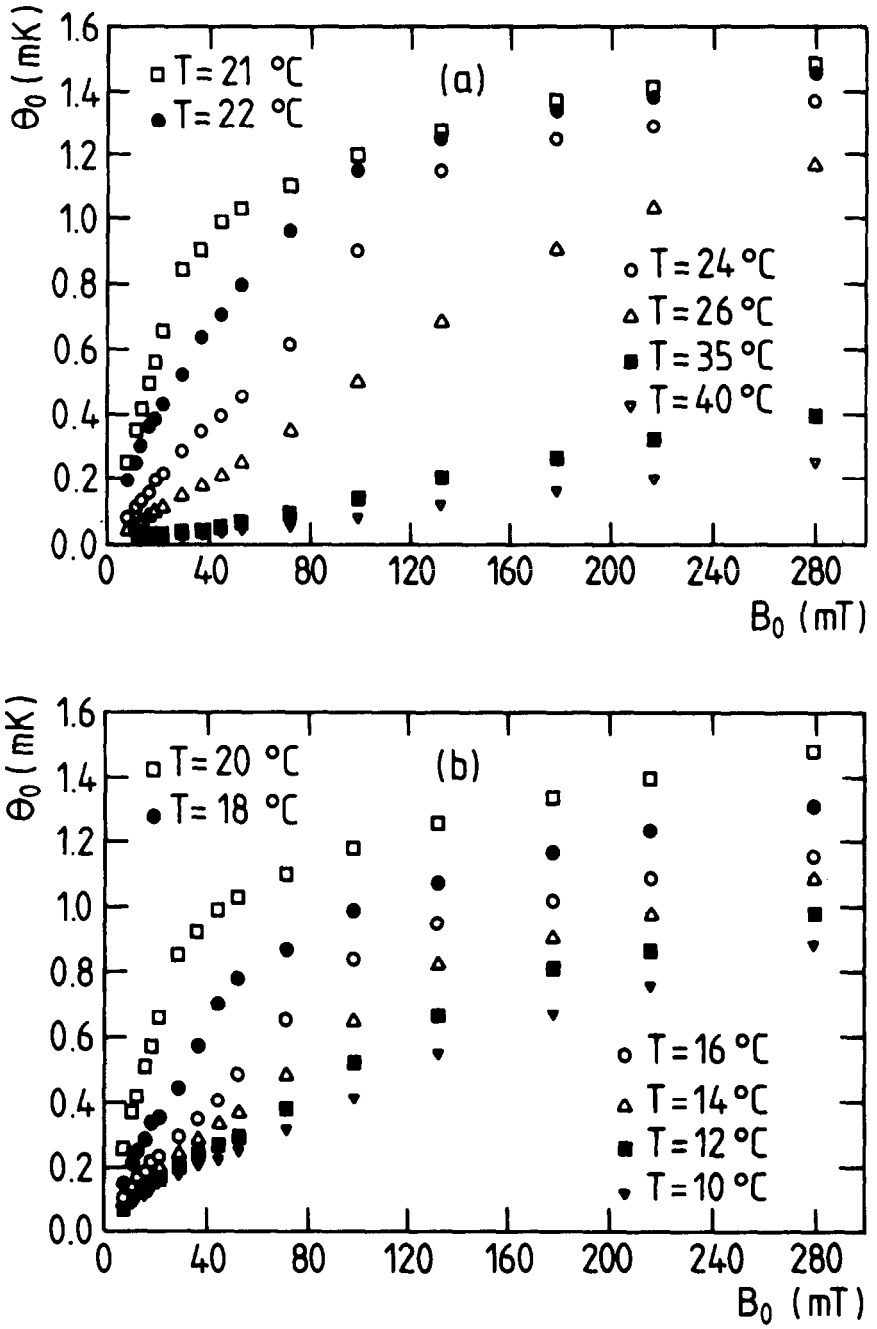


Fig. 4 Field (B_o) dependence of the amplitude θ_o for several isotherms above (a) and below (b) the Curie temperature (T_c = 20.9 °C) of gadolinium

zero average spontaneous magnetization.

The limiting temperature and field dependence of these quantities along certain thermodynamic paths can be expressed in terms of power laws with critical exponents related by scaling law relations (Stanley, 1971). For the field dependence of M and C_B along the critical isotherm, one has :

$$M(T_c,B) = mB^{1/\delta}, \tag{8}$$

$$C_B(T_c,B) = aB^{-\alpha/\beta\delta} + C_0, \tag{9}$$

with C_0 the non-magnetic background heat capacity and a and m critical apmlitudes, δ is the critical exponent describing the shape of the M(B) critical isotherm, β is the critical exponent describing the shape of the spontaneous magnetization curve (B = 0) below the Curie point, α is the characteristic exponent for the specific heat capacity anomaly. The temperature dependence of the specific heat capacity in zero field is given by :

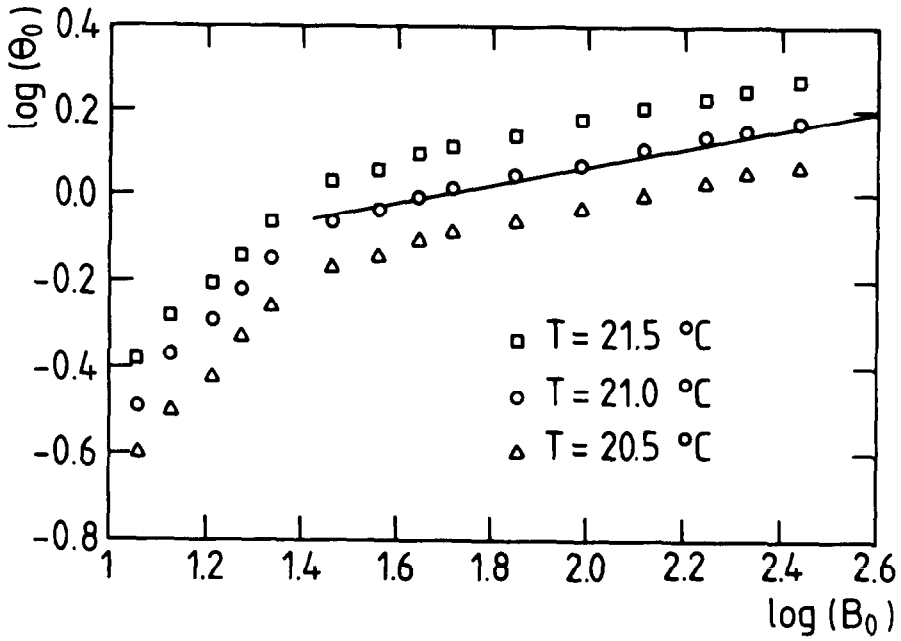
$$C_B(T) = A_{\pm} \left| \frac{T - T_c}{T_C} \right|^{-\alpha} + C_0 \tag{10}$$

where the plus and minus sign, respectively, indicate above or below the critical temperature. An other relevant quantity here is the isothermal susceptibility in zero field for which one has the following power law expression :

$$\chi_T = \left(\frac{\partial M}{\partial B} \right)_T = \Gamma_{\pm} \left| \frac{T - T_c}{T_c} \right|^{-\gamma} \tag{11}$$

Actual values for the different critical exponents depend on the universality class of the critical point investigated. From a review of the experimental values by Chowdhury (1986) it follows that for gadolinium some values are in agreement with the theoretical results for the Ising universality class, while other values agree better with the theoretical results for the Heisenberg universality class. Theoretical values for some critical exponents are given in table 1 for these two universality classes.

On the basis of their experimental results for $(T_c - T)/ T_c > 10^{-3}$ Chowdhury et al. find a ß value in favour of the Heisenberg model. They, however, do not exclude crossover to an other universality class for smaller reduced temperatures. The fact that a negative value is found for the critical exponent α seems to point in the direction of the Heisenberg universality class (Lewis, 1970, Simons and Salomon, 1974, Lanchester et al.,1985).



5 Double logarithmic plot of the amplitude θ_0 versus the static field B_0 for ne critical isotherms

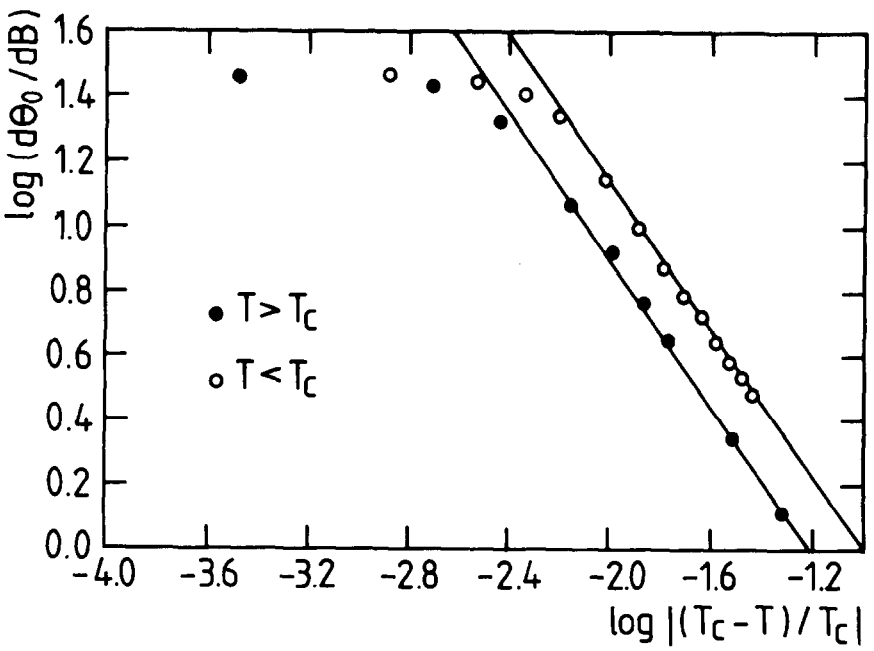


Fig. 6 Double logarithmic plot for the slope of $\theta_0(B_0)$ isotherms versus the reduced temperature difference $|T - T_c|/T_c$

TABLE 1

Theoretical values for some critical exponents[a].

Exponent	Ising model	Heisenberg model
α	+ 0.110±0.002	−0.116±0.002
β	+ 0.325±0.002	+0.365±0.002
γ	+ 1.241±0.002	+1.387±0.004
δ	+ 4.816±0.003	+4.797±0.003

[a] From Le Guillou and Zinn-Justin, 1977, 1985

Inserting (8) and (9) in equation (6) gives :

$$\theta_0 = \rho^{-1}B_1 m B_0^{1/\delta}(aB_0^{-\alpha/\beta\delta} + C_0)^{-1} \tag{12}$$

In the limit B→0 and neglecting C_0 gives $(\alpha + \beta)/\beta\delta$ as a critical exponent for the field dependence of θ_0. Theoretical Heisenberg and Ising values are, respectively, 0.142 and 0.278. In figure 5 we have plotted θ_0 for three near critical isotherms versus B_0 in a double logarithmic scale, in which case one should obtain a straight line with a slope corresponding to the critical exponent. For $B_0 > 25$ mT nearly straight lines are obtained. The line in that figure has a slope of 0.22, which is in between the Ising and the Heisenberg $(\alpha + \beta)/\beta\delta$ value. If however, C_0 in the denominator of equation (12) remains large, one would not expect an exponent $(\alpha + \beta)/\beta\delta$ for θ_0 but rather $1/\delta$, in which case one has a nearly equal value of 0.208 for the Ising and the Heisenberg model. The data below 25mT show substantial curvature. This is probably due to rounding off effects, possibly related also to demagnetization effects (Griffiths, 1969, Kamilov, 1983).

Since according to equation (6),θ_0 and M are proportional one can relate the field dependence of θ_0 for $B_0 \to 0$ to the susceptibility χ_T in the following way :

$$\left(\frac{\partial\theta_0}{\partial\delta B_0}\right)_T = B_1\frac{\partial}{\partial B_0}\left(\frac{M}{\rho C_B}\right)_T \cong \frac{B_1}{\rho C_B}\chi_T(T,B=0) \tag{13}$$

The last result is only valid if one can neglect the field dependence of C_B (and ρ) for $B_0 \to 0$. With the power law expressions (10) and (11) one has :

$$\left(\frac{\delta\theta_0}{\delta B_0}\right) = \rho^{-1}B_1\Gamma_\pm\left|\frac{T - T_c}{T_c}\right|^{\gamma}\left(A\pm\left|\frac{T - T_c}{T_c}\right|^{-\alpha} + C_0\right)^{-1} \tag{14}$$

In the limit of the critical point (neglecting C_0) this results in a divergence with an exponent $(\gamma - \alpha)$ with a theoretical Ising value of 1.13 and a Heisenberg value of 1.503. (In the mean field case one would have $\alpha = 0$ and $\gamma = 1$).

From the isothermal $\theta_0(B_0)$ results (figure 4) we have graphically determined the slope for $B_0 \to 0$. The results are plotted in a double logarithmic scale in

figure 6. Close to T_c there is clearly rounding off, resulting in a finite value at T_c ,but for reduced temperatures larger than 4 x 10^{-3} both the data above and below T_c, fall on a straight line with a slope close to 1.15. This value which is, however, rather uncertain, is closer to the Ising value for $(\gamma - \alpha)$ than to the Heisenberg one. Neglecting C_0 and the field dependence of C_B could also have an effect on this result.

We also want to point out here that a straightforward application of equation (3), identifying dT with θ_0 and dB with B_1 results in a temperature and field dependence of θ_0 which is inconsistent with the experimental results. For the critical isotherm e.g. one can show (J. Rogiers, private communication, 1990) that $(\partial M / \partial T)_B$ has a power law behavior as a function of the magnetic field with an exponent $(\beta - 1)/\beta\delta$. Since $\beta < 1$ this means a divergence at the Curiepoint. For θ_0 this would give an exponent $(\alpha + \beta - 1)/\beta\delta$, which is still negative, resulting in a divergence of $\theta_0(T_c, B_0)$ for B_0going to zero. This is in contradiction with the θ_0 results in figure 4 showing also θ_0 going to zero when B_0 is going to zero.

SUMMARY AND CONCLUSIONS

In this paper we presented a new acoustic detection technique for small periodic temperature variations induced by small periodic magnetic field variations imposed on a magnetic material. The small periodic field modulation can be imposed on a (large) static field resulting in information on the magentic equation of state. Results are presented for gadolinium near the Curie point. The experimental data can be described with an expression derived in the framework of the Rosencwaig-Gersho (photoacoustic) theory for uniform sample heating.

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