

INVESTIGATION OF PARAMAGNETIC SATURATION IN LANTHANUM MANGANESE NITRATE

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Received 10 May 1972

Synopsis

Paramagnetic saturation of lanthanum manganese nitrate, $\text{La}_2\text{Mn}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$, has been investigated at liquid He temperatures in a static as well as a dynamical way. With the aid of the molecular-field theory the Casimir and Du Pré dispersion and absorption curves are adapted explicitly to the phenomenon of saturation. A satisfactory agreement has been observed between theory and experiment.

1. *Introduction.* The main purpose of the investigations to be described was to verify experimentally some relations that can easily be calculated from classical paramagnetic theory and molecular-field theory. In order to obtain a reasonable degree of saturation in our experiments, lanthanum manganese nitrate (abbreviation LMnN) was used, because for the Mn^{++} ion $S = 5/2$. This ion has the additional advantage that $L = 0$, so that no orbital angular momentum has to be taken into account. The influence of paramagnetic saturation on the Casimir and Du Pré formulas was firstly considered by De Haas and Du Pré¹). Their work has been extended by Van den Broek *et al.*²). They made use of approximations which could reasonably describe their experiments. In this paper we derive some formulas that describe the experimental results in a more nearly exact way. Two kinds of susceptibility measurements were performed: static measurements by means of a Faraday balance, and dynamic measurements by means of a mutualinductance bridge. In the first set of experiments $\chi(T, H, \nu = 0)$ was determined, in the second set $\chi'/\chi_0(T, H, \nu)$ and $\chi''/\chi_0(T, H, \nu)$ were obtained.

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2. *Samples.* The chemical formula of LMnN is $\text{La}_2\text{Mn}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$. It is supposed to have the same structure as cerium magnesium nitrate. The space group of this substance, $R\bar{3}$, was determined by Zalkin³). There are three $[\text{Mn}(\text{H}_2\text{O})_6]^{++}$ complexes per unit cell. One of the three Mn^{++} ions per unit cell has symmetry $\bar{3}$ (site I), whereas the other two have only symmetry 3 (site II). The molar weight of LMnN is 1619, the approximate density $2 \times 10^3 \text{ kg/m}^3$.

The a.c. measurements were performed perpendicular to the triad axis on a cylinder of 20 mm length and 6.5 mm diameter, weighing 1.325 g. For the d.c. measurements a small crystal of 10.1 mg was used, in this case the field pointed along an arbitrary direction.

3. *Experimental methods.* For the a.c. experiments a Hartshorn mutual-inductance bridge was used, which automatically records χ' vs. H and χ'' vs. H curves at fixed frequency and temperature⁴). As soon as sufficient graphs of this kind are available, sets of $\chi'(\nu)$ and $\chi''(\nu)$ curves can be constructed. External fields, up to $1.75 \times 10^6 \text{ A/m}$ (22 kOe), were generated by a superconducting coil. Frequencies between 1.5 and 3000 Hz were used, and temperatures were varied between 2.06 and 4.24 K.

From the $\chi'(\log \nu)$ and $\chi''(\log \nu)$ curves, the following information can be obtained: firstly, the limiting value of χ' for $\nu \rightarrow 0$ gives the information about the degree of paramagnetic saturation. Secondly, the relaxation behaviour as a function of field and temperature can be studied. This subject will be discussed elsewhere⁵). Thirdly, the limiting values for $\nu \rightarrow \infty$ of the $\chi'(\log \nu)$ curves at different H give information about the specific heat of the sample.

The d.c. measurements were performed with a Faraday balance, described by Gijsman⁶). The magnetization of LMnN was determined at six temperatures between 1.2 and 4.2 K, and at field strengths between 1.35×10^5 and $14 \times 10^5 \text{ A/m}$ (1.7 to 17.6 kOe).

4. *Theory.* The magnetization M is given by the well-known Brillouin formula:

$$M = Ng\beta SB_S(x), \quad x = \mu_0 g\beta SH/kT, \quad (1)$$

The field H , acting on the ions, is given in the molecular-field theory by:

$$H = H_{\text{ext}} + \gamma M, \quad (2)$$

where H_{ext} is the external field. For small argument x ,

$$B_S(x) = \frac{S+1}{S} \frac{x}{3}. \quad (3)$$

The differential susceptibility at zero frequency may be written as:

$$\chi_0(H) = \left(\frac{\partial M}{\partial H_{\text{ext}}} \right)_T. \quad (4)$$

Differentiation of (1) with respect to H_{ext} gives:

$$\chi_0(H) = Ng\beta SB'_S(x) (\mu_0 g\beta S/kT) [1 + \gamma\chi_0(H)] \quad (5)$$

and, solving for $\chi_0(H)$:

$$\chi_0(H) = \frac{(C/T) D(x)}{1 - (\theta/T) D(x)}. \quad (6)$$

Here, the Curie constant C equals $\mu_0 Ng^2\beta^2 S(S+1)/3k$, $\theta = \gamma C$ and $D(x) \equiv B'_S(x)/B'_S(0)$. Then,

$$K \equiv \frac{\chi_0(H)}{\chi_0(0)} = D(x) \frac{1 - (\theta/T)}{1 - (\theta/T) D(x)}. \quad (7)$$

Further, we define a quantity V :

$$V \equiv \frac{D(x)}{1 - (\theta/T) D(x)}. \quad (8)$$

The well-known relations of Casimir and Du Pré for dispersion and absorption are:

$$\frac{\chi'}{\chi_0(H)} = 1 - F + \frac{F}{1 + \omega^2\tau^2}; \quad F = \frac{C_H - C_M}{C_H}, \quad (9)$$

$$\frac{\chi''}{\chi_0(H)} = \frac{F\omega\tau}{1 + \omega^2\tau^2}. \quad (10)$$

In (9), C_H and C_M are the specific heat at constant field and magnetization, respectively. It can easily be shown that:

$$C_H - C_M = \mu_0 C (H^2/T^2) \frac{D(x)}{1 - (\theta/T) D(x)}. \quad (11)$$

Combining (7), (8) and (11) with (9) and (10), and supposing that $C_M = b/T^2$, one obtains:

$$\frac{\chi'}{\chi_0(0)} = \frac{bK}{b + \mu_0 CH^2 V} + \frac{\mu_0 CH^2 VK}{b + \mu_0 CH^2 V} \frac{1}{1 + \omega^2 \tau^2}, \quad (12)$$

$$\frac{\chi''}{\chi_0(0)} = \frac{\mu_0 CH^2 VK}{b + \mu_0 CH^2 V} \frac{\omega \tau}{1 + \omega^2 \tau^2}. \quad (13)$$

From the formulas (12) and (13) the following predictions can be made.

- a. The limiting value of the dispersion curve for $\omega \rightarrow 0$ should be K .
- b. The limiting value r of the dispersion curve for $\omega \rightarrow \infty$ should be

$$r = \frac{bK}{b + \mu_0 CH^2 V},$$

so that

$$\frac{1}{V} \frac{K - r}{r} = \frac{\mu_0 C}{b} H^2. \quad (14)$$

- c. The height h of the absorption curve at $\omega = \tau^{-1}$ should be

$$h = \frac{1}{2} \frac{\mu_0 CH^2 VK}{b + \mu_0 CH^2 V},$$

and consequently:

$$\frac{1}{V} \frac{2h}{K - 2h} = \frac{\mu_0 C}{b} H^2. \quad (15)$$

- d. From (14) and (15) it follows that:

$$K = r + 2h. \quad (16)$$

The relations (14), (15) and (16) will be compared with the experimental results; besides, both (14) and (15) permit the determination of b .

5. *Results.* 5.1. In static fields. We obtained a set of $M(H)$ curves at six different temperatures between 1.2 and 4.2 K. From the initial slopes $\chi(0)$ the Weiss constant ($\theta = -0.46$ K) as well as the Curie constant ($C = 1.69 \times 10^{-4}$ $\text{K m}^3/\text{mol}$) were derived, using the Curie-Weiss law $\chi = C/(T - \theta)$. The value of C agrees satisfactorily with the "g = 2 value" of the Curie constant, 1.65×10^{-4} $\text{K m}^3/\text{mol}$.

From (1), (2) and (3) it is easily seen that:

$$x = x_0 + \frac{\theta}{T} \frac{B_S(x)}{B_S'(0)}, \quad (17)$$

if $x = \mu_0 g \beta S H / k T$ and $x_0 = \mu_0 g \beta S H_{\text{ext}} / k T$. Note that $B_S'(0)$ is simply $(S + 1)/3S$. Now, for every given point with some H_{ext} and T , x can be determined either by a simple iteration process or graphically, using the above-mentioned value of θ . Since the magnetization has to obey the law $M = N g \beta S B_S(x)$, a plot of M vs. x of all the available experimental points should give a Brillouin curve. Fig. 1

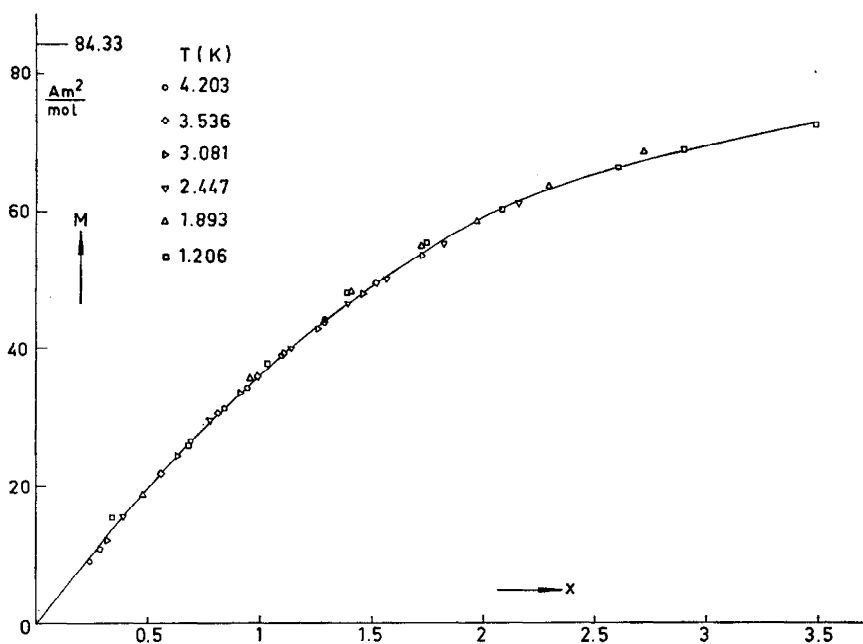


Fig. 1. The static magnetization of lanthanum manganese nitrate as a function of the quantity $x = \mu_0 g \beta S H / k T$. The experiments obey the law $M = N g \beta S B_S(x)$ within the limits of the experimental accuracy.

shows that this is true to a fair degree. The experimental and theoretical values of the constant $N g \beta S$, 84.3 and 83.76 Am^2/mol , respectively, are equal within the limits of the experimental accuracy. Finally, the relation $\theta = 2zJS(S + 1)/3k$ gives $zJ/k = -0.079$ K. In this molecular-field relation, z is the number of nearest neighbours and J the exchange constant.

5.2. In alternating fields. With this method, a value $\theta = -0.45$ K has been determined for the Weiss constant. The results $\theta = -0.46$ K and -0.45 K, respectively, may be compared with $\theta = -0.42$ K, found by Mess⁷⁾ and $\theta = -0.49$ K, found by Sapp⁸⁾. Rather than with relaxation phenomena, we shall be concerned here with the behaviour of the system at very low and at very high

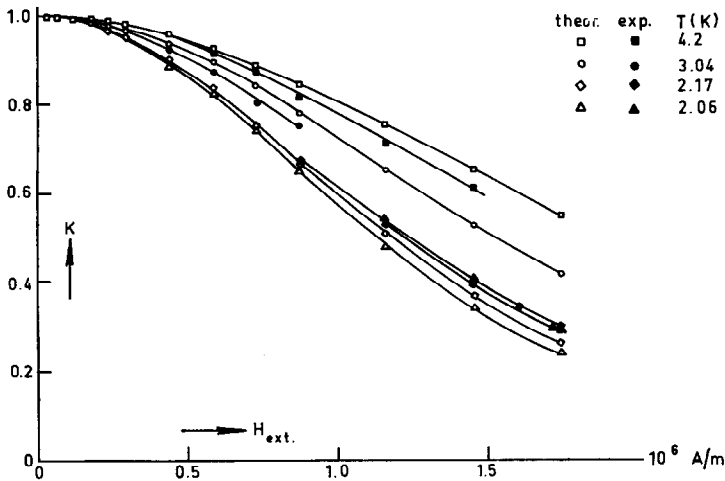


Fig. 2. Experimental and theoretical values of $K = \chi'(H)/\chi'(0)$ for $\nu \rightarrow 0$ as a function of the magnetic field, at four different temperatures.

frequencies. In fig. 2 the experimental values of $\chi'(H)/\chi'(0)$ and the theoretical values of K have been plotted as a function of the external field. Agreement between the two kinds of curves is reasonable, considering the difficulty of extrapolating the $\chi'(H)$ curve to $\nu = 0$.

Fig. 3 shows $\log(K - r)/Vr$ and $\log 2h/V(K - 2h)$ as a function of the logarithm of the applied magnetic field. According to (14) and (15), the slopes of the curves should be 2. The experimental values are 2.00 and 1.94, respectively. From both graphs the value of $\mu_0 C/b$ and thus of b/R per gram ion can be determined. For the latter quantity we found 0.081 K^2 and 0.085 K^2 , respectively, giving an average value for b/R of 0.083 K^2 . Mess⁷⁾ quotes $b/R = 0.060 \text{ K}^2$, and Sapp⁸⁾ 0.070 K^2 .

In fig. 4 a verification is made of (16) by plotting $2h$ vs. $K - r$. Agreement between experiments and the theoretical (dashed) line is very good, except for the highest field strengths at temperatures above the lambda point T_λ (2.17 K). The same remark applies for figs. 2 and 3. The deviations can be partly understood: firstly, the quantity r is very small and therefore relatively uncertain for large fields. Secondly, since the heat conductivity in the crystal and between liquid and crystal

is finite, the absorption curve is often broadened, resulting in a relatively small value for h . In fact, our measurements do show that the absorption curve becomes progressively broader than the Casimir and Du Pré formulas predict as the field strength increases. The fact that agreement with theory for $T < T_\lambda$ is more satisfactory than for $T > T_\lambda$ gives further support to this explanation.

Using the formulas $b = \mu_0 Ch^2$ and $\mu h = \alpha k T_c$, where h is the so-called internal field, μ the magnetic moment per ion, T_c the temperature of the magnetic phase

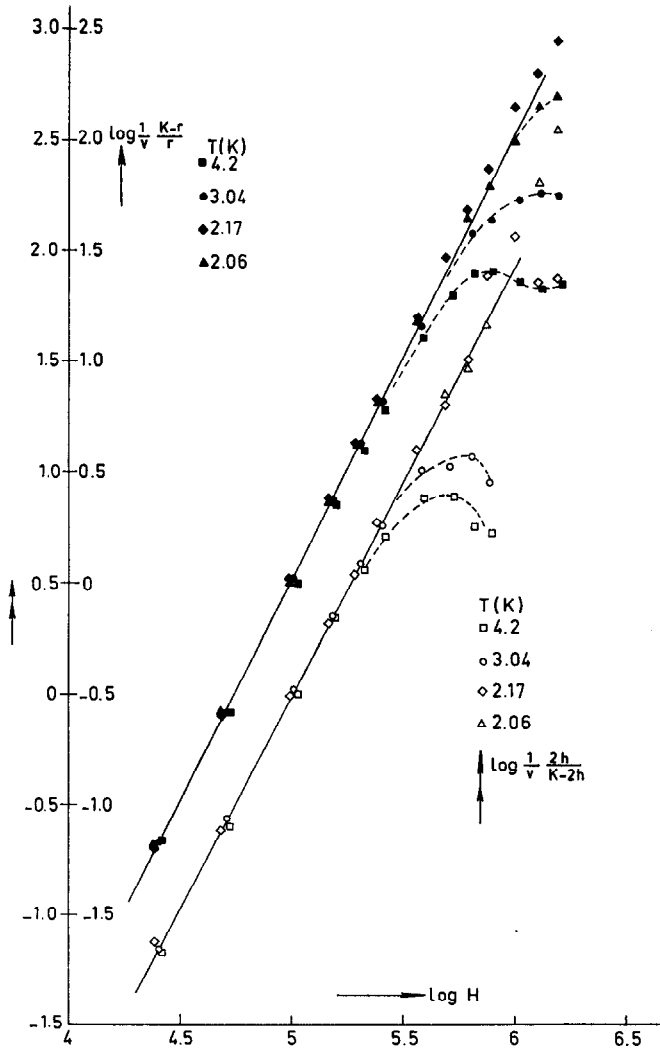


Fig. 3. Plots of $\log (K - r)/Vr$ vs. $\log H$ and $2h/V(K - 2h)$ vs. $\log H$, to verify the formulas (14) and (15). The left-hand scale corresponds to the right-hand graph, as indicated by the double arrows.

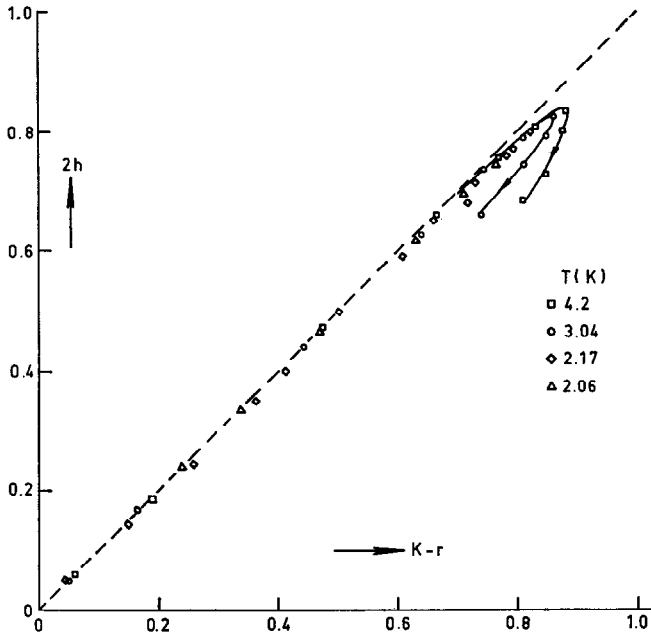


Fig. 4. A verification of formula (16). The experiments should be described by the dashed line $2h = K - r$.

transition, and α a constant of order unity, one can predict that for two different substances:

$$b_1/b_2 = T_{c_1}^2/T_{c_2}^2. \tag{18}$$

Taking 1 as LMnN and, for instance, 2 as CMN (cerium magnesium nitrate), and using the values of Mess⁷⁾ for b_2 , T_{c_1} (0.230 K) and T_{c_2} (0.0019 K), the left-hand part equals 14×10^3 , the right-hand part 15×10^3 . This is a good result for such a rough estimation.

One can further estimate the effective number of nearest neighbours z and the average exchange constant J , by applying several corrections to the overall value of b/R^7) to retain the exchange part of the specific heat, and combining the Van Vleck⁹⁾ formula $C_M/R = (2z/3) [JS(S + 1)/kT]^2$ for the exchange specific heat with the corrected value of b/R and the relation $zJ/k = -0.079$ K. The result is: $z = 5.0$ and $J = -0.016$ K. It should be emphasized that there are two sites for the Mn^{++} ions, so the numbers for z and J , mentioned above, are mean values for the two sites.

In conclusion, one may state that the magnetic behaviour of LMnN can be well described with the molecular-field theory. The deviations between theory and experiment can be understood qualitatively.

Acknowledgements. We are much indebted to Drs. L. J. M. van de Klundert for his permission to use the improved Hartshorn bridge, and for his guidance during the measurements. The authors are very grateful to Professor B. S. Blaisse for his encouragement and stimulating discussions. Professor J. van den Handel of Leiden University was so kind to permit the measurements with the Faraday balance, and we are grateful to Drs. S. R. Brouwer for his participation in these experiments. Finally, we wish to express our sincere thanks to the technicians of the three laboratories that were involved for their indispensable aid.

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