Investigations of the nonlinear paramagnetic effect in $HgCr_2Se_4$ near the Curie temperature

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Experimental results of the nonlinear paramagnetic effect (NPE) in $HgCr_2Se_4$ for temperatures T_c+3 K $< T < T_c+40$ K obtained in external magnetic fields parallel or perpendicular to the measuring field are presented. For the same configurations of measuring and external fields the paramagnetic susceptibility versus temperature is also investigated. The exponent in the relation $\Delta\chi/B_{\mathrm{EXT}}^2 \sim (T-T_c)^{-5.1}$ has been determined; the method of determining the Curie temperature is given. With a basis on the Langevin theory of paramagnetism and Debye-Herweg nonlinear-dielectric-effect theory, interpretations are presented of the experimental data obtained. From measured values of paramagnetic susceptibility and NPE, the mean values of the resultant magnetic moment of the ordered region (pretransition fluctuation), as well as the mean number of such fluctuations per mole for various temperatures, have been determined.

I. INTRODUCTION

The temperature dependence of paramagnetic susceptibility in the pretransition region of the paraferromagnetic phase transition is mainly determined by fluctuations. Taking into account these fluctuations, which are understood to be the tendency to the formation of momentary regions of magnetic ordering, makes it possible to explain the existence of the high values of magnetic susceptibility in $HgCr_2Se_4$ above the Curie temperature. The nonhomogeneity of the magnetic ordering is also the source of strong nonlinear effects in the pretransition region, as is evidenced by the high values of the nonlinear paramagnetic effect (NPE).[1] From measurements of NPE and paramagnetic susceptibility, and with a basis on the Langevin theory of paramagnetism and Debye-Herweg[2] nonlinear dielectric effect (NDE) theory, it becomes possible to determine the mean value of the resultant magnetic moment of an ordered region and also the mean number of such regions per mole of the substance, representing pretransition fluctuations, at various temperatures. The NPE theory is based on the mathematical description of the analogous effect in dielectrics, i.e., the nonlinear dielectric effect.[2] Making use of the NPE method, however provides broader experimental possibilities, particularly when performing measurements with various configurations of magnetic fields, i.e., measuring field and external field, causing variations in susceptibility. The construction of an effective measuring system with nonparallel electric fields presents serious difficulties. Hence the NPE measurements made in perpendicular fields represent the first measurements, also allowing the verification of certain results in the theory of nonlinear dielectric effect.[3]

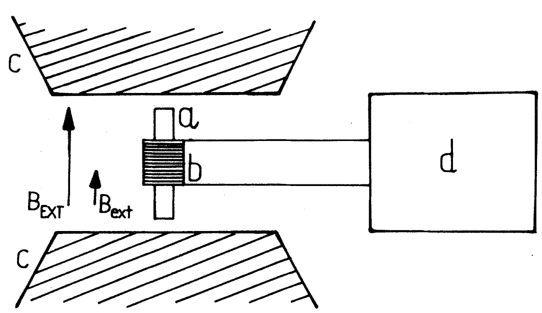

FIG. 1. Measuring system: (a) sample, (b) solenoid generating measuring field, (c) electromagnet generating the fields inducing susceptibility variations, (d) system recording susceptibility values and variations.

II. MEASURING METHOD AND RESULTS

For an isotropic medium, the paramagnetic susceptibility as a function of magnetic field may be written in the form of the following series:

$$\chi=\chi_0+\chi_2 B^2+\cdots . \quad (1)$$

With the use of the measuring system shown in Fig. 1, simultaneous measurements of χ_0 and $\Delta\chi=\chi-\chi_0$ were made. A beat apparatus with Wehnelt cylinder oscilloscope modulation was used to record the measured values.[4] Measurements were made on polycrystalline samples. For an analysis of the measured values of paramagnetic susceptibility χ_0 and of $\Delta\chi/B_{\mathrm{EXT}}^2$, for samples in the form of long cylinders, the demagnetization effect was taken into account using the method described in Refs. 5 and 6. As measurements were carried out in a measuring field of frequency 1 MHz, which for $HgCr_2Se_4$ is situated below the dispersion band, measured values were taken as static. The nonlinear paramagnetic effect method used for measurements depends on recording variations in magnetic susceptibility $\Delta\chi=\chi-\chi_0$ (Fig. 1), induced due to applying an external magnetic field using an electromagnet having an induction B_{EXT}, such that in the expansion of the series [Eq. (1)] terms of higher order than the quadratic may be neglected. χ_0 denotes susceptibility for $B_{\mathrm{EXT}}=0$, χ susceptibility for $B_{\mathrm{EXT}}\neq 0$. With reduction in temperature, the range of B_{EXT} values for which susceptibility is a quadratic function of magnetic field is also reduced.

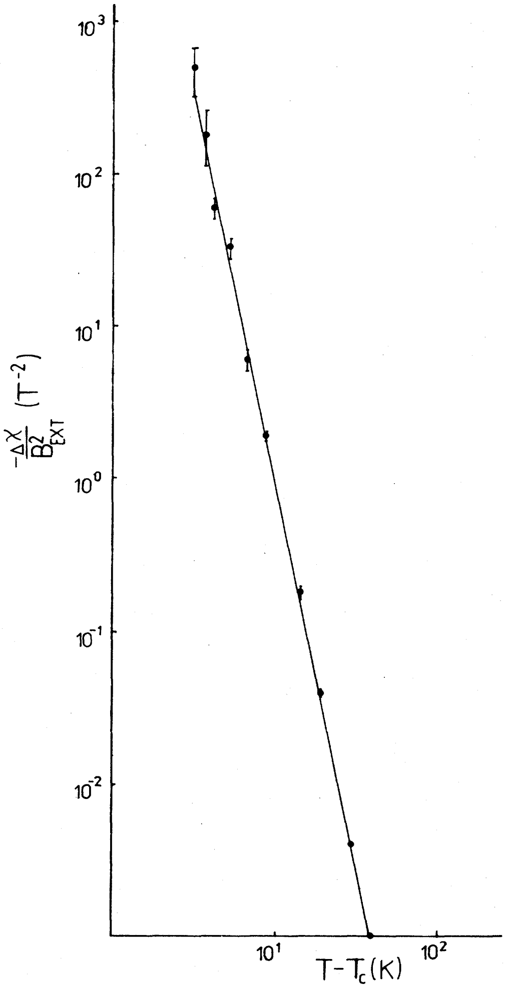

FIG. 2. Log-log function of $\Delta\chi/B^2_{\mathrm{EXT}}$ vs $(T-T_c)$ for a measuring field parallel to the field of the electromagnet (sample in the form of a long cylinder).

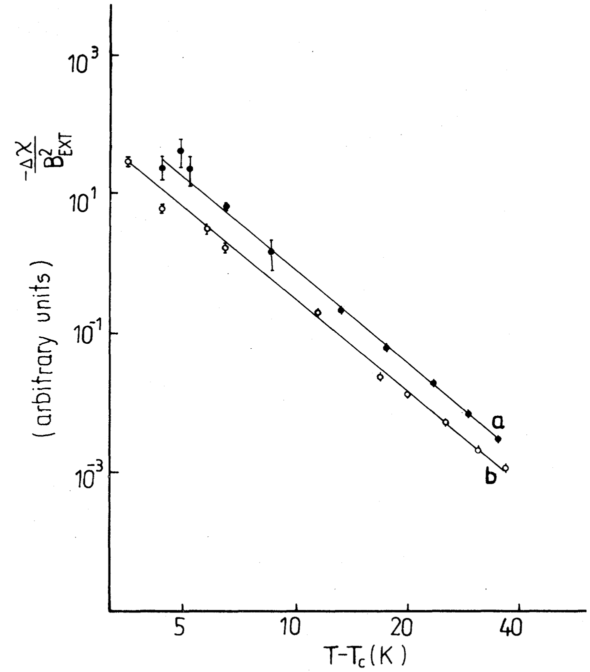

FIG. 3. Log-log function of $\Delta\chi/B^2_{\mathrm{EXT}}$ vs $(T-T_c)$ for the spherical sample: (a) measuring field parallel to the external electromagnet field, (b) measuring field perpendicular to the external electromagnet field.

In practice $\Delta\chi$ was measured for a few values of B_{EXT}. With a basis on the linear relation between $\Delta\chi$ and B^2_{EXT}, the value of $\Delta\chi/B^2_{\mathrm{EXT}}$ was determined as the slope of the straight line obtained. Figure 2 shows the log-log function of $\Delta\chi/B^2_{\mathrm{EXT}}$ vs $(T-T_c)$ for a measuring field $\vec{B}_{\mathrm{ext}}$ parallel to the field of the electromagnet. Within the limits of error this has a linear form. From this the following relation was found:

$$\frac{\Delta\chi}{B^2_{\mathrm{EXT}}} \sim (T-T_c)^{-5.1} . \quad (2)$$

Figure 3 gives the results of measurements of $\Delta\chi/B^2_{\mathrm{EXT}}$ as a function of $(T-T_C)$ on a log-log scale for parallel and perpendicular settings of measuring field $\vec{B}_{\mathrm{ext}}$ and external electromagnet field $\vec{B}_{\mathrm{EXT}}$. In the case $\vec{B}_{\mathrm{ext}} \| \vec{B}_{\mathrm{EXT}}$, the value $\Delta\chi/B^2_{\mathrm{EXT}}$ is approximately 3 times greater than in the case of $\vec{B}_{\mathrm{ext}} \perp \vec{B}_{\mathrm{EXT}}$, throughout the whole range of temperatures. This is in agreement with the theoretical result obtained in Ref. 3 for the nonlinear dielectric effect.

Apart from measurements of χ_0 and $\Delta\chi/B^2_{\mathrm{EXT}}$, a study was also made of magnetic susceptibility as a function of temperature for samples placed in the electromagnet field $\vec{B}_{\mathrm{EXT}}$ both parallel and perpendicular to the measuring field. Measurements were performed for various values of magnetic fields B_{EXT} in the interval from 0 to $0.5T$. Figure 4 shows the function $\chi(T)$ in parallel fields. In a certain range of values of the magnetic fields, the form of the $\chi(T)$ curve exhibits distinct maxima and minima. With an increase in induction $B^{\|}_{\mathrm{EXT}}$, the distance between extreme values of susceptibility, also increases.

Figure 5 was prepared from measurements of function $\chi(T)$ in weak fields $(B^{\|}_{\mathrm{EXT}} \leq 0.015T)$. Segments are marked on the figure for particular values of $B^{\|}_{\mathrm{EXT}}$, corresponding to the temperature intervals for which $(\partial\chi/\partial T)_B \geq 0$. Since for $B^{\|}_{\mathrm{EXT}}=0$, no temperature region was found in which the susceptibility increased or remained constant with increase in temperature, it was assumed that for $B_{\mathrm{EXT}}=0$ these segments come to a point with the coordinate of T_c (Refs. 7 and 8). A susceptibility versus temperature function in a magnetic field of such a form was used in these investigations for determination of the Curie point ($T_c = 105.9$ K). An approximation was applied in which the center points of the segments on Fig. 5 determine the path of a straight line which cuts the temperature axis at the point T_c. This method allows the Curie temperature to be ascertained with an accuracy of 0.1 K and also has the advantage that when the effects of demagnetization are not taken into account, the error involved is very small, considerably smaller than in other

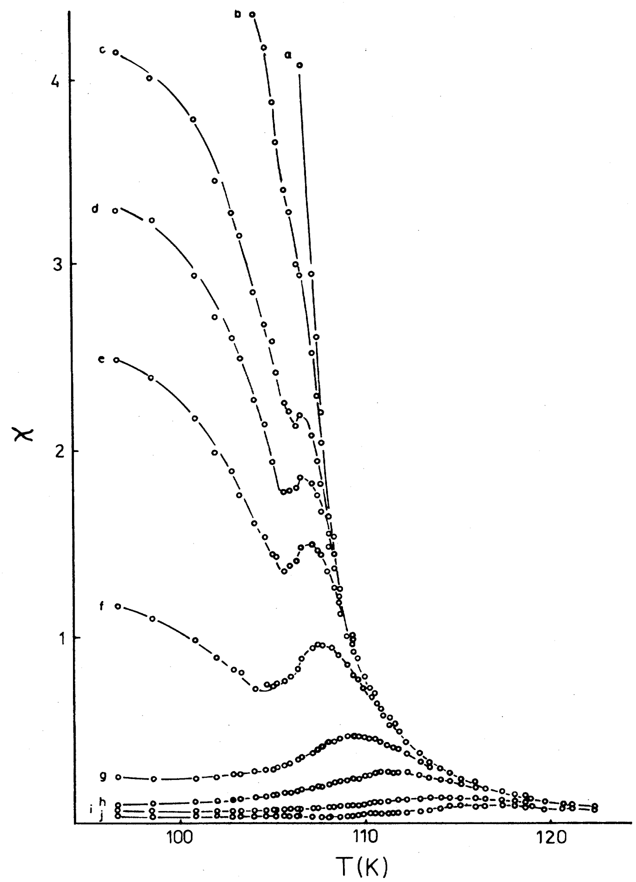

FIG. 4. Function of magnetic susceptibility vs temperature in various external electromagnet magnetic fields $B_{\rm EXT}$ parallel to the measuring field; $B_{\rm EXT}=0.002T$ *a*; $0.005T$ *b*; $0.009T$ *c*; $0.011T$ *d*; $0.015T$ *e*; $0.028T$ *f*; $0.0695T$ *g*; $0.1375T$ *h*; $0.279T$ *i*; $0.4535T$ *j*.

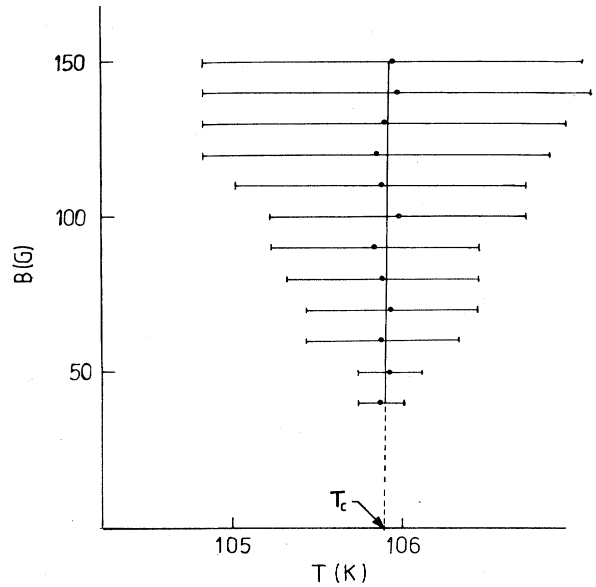

FIG. 5. Method applied to determine the Curie temperature. Central points of segments representing the temperature intervals for which $(\partial \chi/\partial T)_B \geq 0$ determine the straight line cutting the temperature axis at the point T_c.

methods, particularly for powder samples. The fact that this value of the Curie temperature is taken is the reason why the power index in formula (2) is different from that obtained in Ref. 1 for a similar compound, when T_c was determined as the inflection point of the function $\chi(T)$ for $B_{\rm EXT}=0$.

The temperature function $\chi(T)$ for a sample placed in a constant magnetic field $B^{\perp}_{\rm EXT}$ perpendicular to the measur-

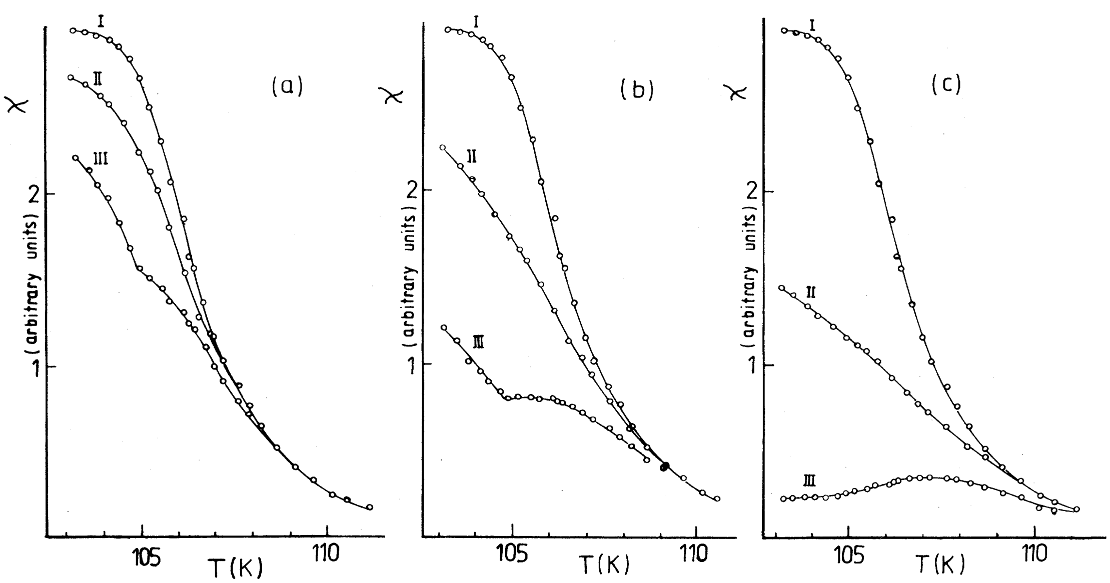

FIG. 6. Magnetic susceptibility vs temperature in electromagnet field parallel to and perpendicular to the measuring field: (a) $B_{\rm EXT}\cong 0$ (I); $B^{\perp}_{\rm EXT}=0.015T$ (II); $B^{\parallel}_{\rm EXT}=0.015T$ (III), (b) $B_{\rm EXT}\cong 0$ (I); $B^{\perp}_{\rm ext}-0.030T$ (II); $B^{\parallel}_{\rm EXT}=0.030T$ (III); (c) $B_{\rm EXT}\cong 0$ (I); $B^{\perp}_{\rm EXT}=0.060T$ (II); $B^{\parallel}_{\rm EXT}=0.060T$ (III).

ing field is different from that measured in a parallel field $B^{\parallel}_{\mathrm{EXT}}$. Figure 6 shows the function $\chi(T)$ for electromagnet fields: $B_{\mathrm{EXT}} \cong 0$; $B^{\perp}_{\mathrm{EXT}} = 0.015T$; $B^{\perp}_{\mathrm{EXT}} = 0.03T$; $B^{\perp}_{\mathrm{EXT}} =$ $0.06T$; $B^{\parallel}_{\mathrm{EXT}} = 0.015T$; $B^{\parallel}_{\mathrm{EXT}} = 0.03T$; $B^{\parallel}_{\mathrm{EXT}} = 0.06T$. Only in the case with parallel fields were local extremes in susceptibility observed on the $\chi(T)$ function. Figure 6 was plotted based on measurements performed on powder samples molded in the form of spheres. Since the effects of demagnetization were not taken into account in the analysis of susceptibility measurement results in external fields (for samples in the shape of long cylinders, this has no basic effect on the form of the curves obtained, but measurements made for spherical samples are only suitable for comparison of the cases $B^{\perp}_{\mathrm{EXT}}$ and $B^{\parallel}_{\mathrm{EXT}}$), the function for $B^{\parallel}_{\mathrm{EXT}}$ (Fig. 6) differs from those in Fig. 4, which were obtained for powder samples in the form of long cylinders. Moreover, for the spherical samples, measurements of relative value of susceptibility were made.

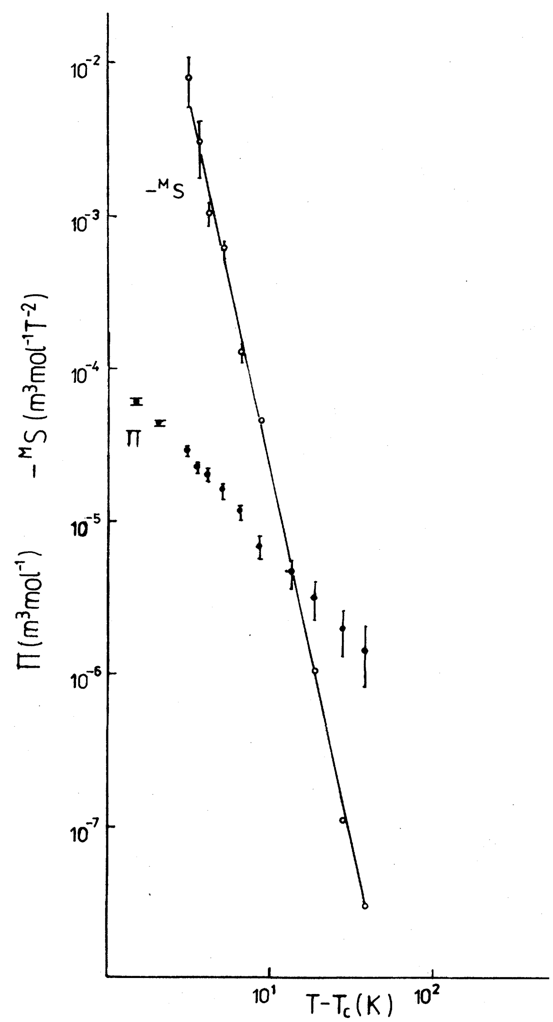

FIG. 7. Values of coefficients Π and ^{M}S as functions of temperature in a log-log scale.

III. DISCUSSION

Treating the nonhomogeneity of magnetic ordering in various parts of the magnetic material as independent fluctuations, and also assuming that the magnetic field orientates only the resultant magnetic moments of ordered regions whilst not affecting their value (this is justifiable for the fields $B_{\mathrm{EXT}} < 0.5T$ used here), the molar magnetization component in the direction of the local measuring field $\vec{\mathbf{B}}_m$ (Fig. 1) may be written as follows:

$$^{M}M(T) = N(T)\mu(T)L\left[\frac{\mu(T)(B+B_m)}{kT}\right] \quad \text{for } \vec{\mathbf{B}} \,||\, \vec{\mathbf{B}}_m \tag{3a}$$

$$^{M}M(T) = N(T)\mu(T)L\left[\frac{\mu(T)(B^2+B_m^2)^{1/2}}{kT}\right]\frac{B_m}{(B^2+B_m^2)^{1/2}} \quad \text{for } \vec{\mathbf{B}} \perp \vec{\mathbf{B}}_m \,. \tag{3b}$$

B_m and B are local fields which, assuming an Onsager local field, are related to the corresponding external fields B_{ext} and B_{EXT} by the equations

$$B_m = \frac{3[\chi(T)+1]}{2\chi(T)+3} B_{\mathrm{ext}}, \tag{4a}$$

$$B = \frac{3[\chi(T)+1]}{2\chi(T)+3} B_{\mathrm{EXT}} \,. \tag{4b}$$

$L(y) = \coth y - y^{-1}$ is a Langevin function. Making use of the Langevin function would appear to be justified due to

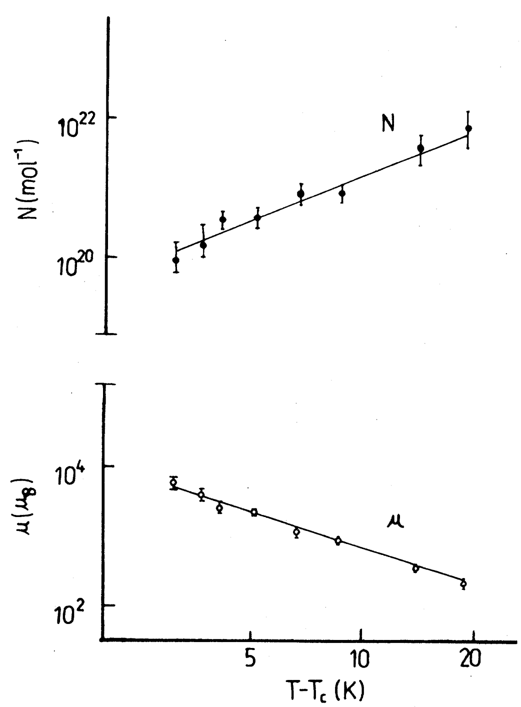

FIG. 8. Value of the resultant mean magnetic moment of the ordered region and mean number of such regions per mole of the substance as a function of temperature on a log-log scale.

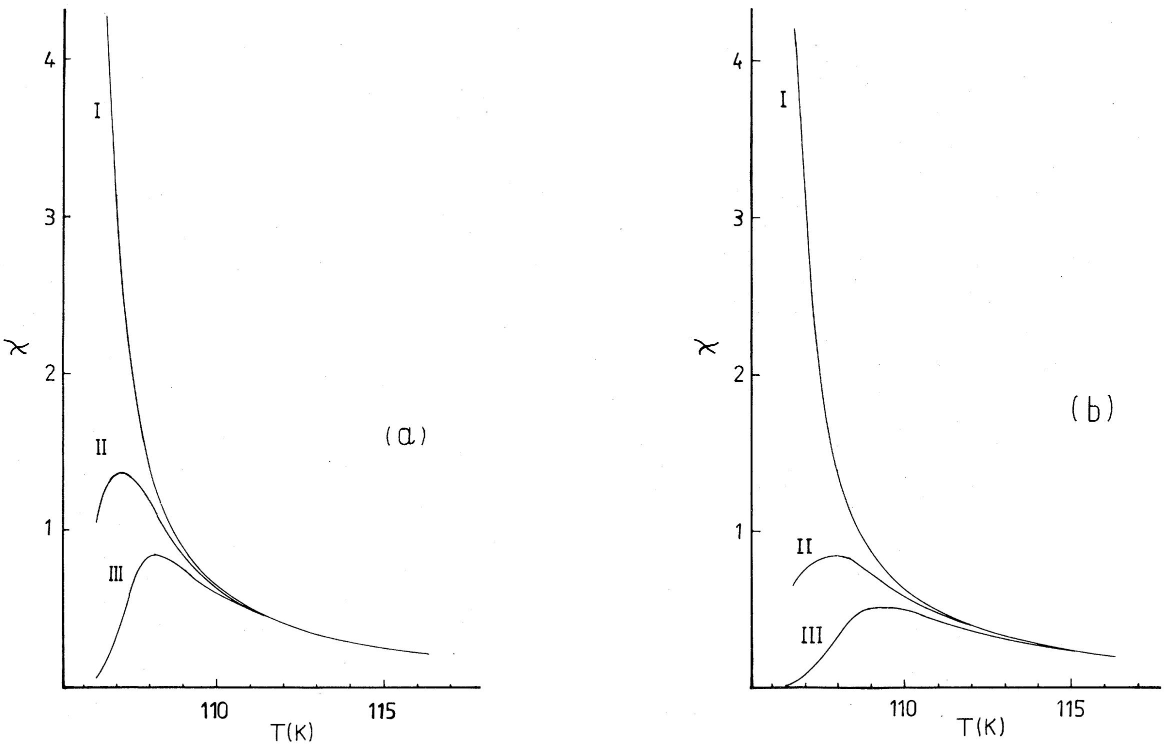

FIG. 9. Magnetic susceptibility as a function of temperature for various magnetic fields determined numerically from formulas (5a) and (5b): (a) $B^{\perp}=B^{\parallel}=0.002T$ (I, curves coincide); $B^{\perp}=0.03T$ (II); $B^{\parallel}=0.03T$ (III), (b) $B^{\perp}=B^{\parallel}=0.002T$ (I, curves coincide); $B^{\perp}=0.06T$ (II); $B^{\parallel}=0.06T$ (III).

the high values of magnetic fluctuation moments. In formulas (3a) and (3b) the influence of magnetic ions not exhibiting fluctuations is neglected. The corresponding expression for molar paramagnetic susceptibility in the experimental conditions, approximately $B \gg B_m$ has the form

$$^{M}\chi=\mu_0\frac{N(T)\mu^2(T)}{kT}\frac{\partial L}{\partial x} \quad \text{for } \vec{B}\parallel\vec{B}_m \tag{5a}$$

$$^{M}\chi=\mu_0\frac{N(T)\mu^2(T)}{kT}\frac{L}{x} \quad \text{for } \vec{B}\perp\vec{B}_m\ , \tag{5b}$$

where

$$x=\frac{\mu(T)B_{\mathrm{EXT}}}{kT}\ ,$$

μ_0 is the permittivity of vacuum.

A. Nonlinear paramagnetic effect

Expanding the expressions (5a) and (5b) in a series relative to the external magnetic field with an accuracy to the quadratic term, gives the following for the case $\vec{B}\parallel\vec{B}_m$:

$$^{M}\chi(T)=\alpha(T)\Pi(T)+\beta(T)\,^{M}S(T)B_{\mathrm{ext}}^2\ , \tag{6a}$$

and the following for the case $\vec{B}\perp\vec{B}_m$;

$$^{M}\chi(T)=\alpha(T)\Pi(T)+\tfrac{1}{3}\beta(T)\,^{M}S(T)B_{\mathrm{ext}}^2\ , \tag{6b}$$

where the coefficients are given by

$$\Pi(T)=\frac{\mu_0 N(T)\mu^2(T)}{9kT}\ , \tag{7a}$$

$$^{M}S(T)=-\frac{\mu_0 N(T)\mu^4(T)}{45k^3T^3}\ . \tag{7b}$$

The factors determining the local fields have the form

$$\alpha(T)=\frac{[\chi_0(T)+1]9}{2\chi_0(T)+3}\ ,$$

$$\beta(T)=\frac{\{3[\chi_0(T)+1]\}^4}{[2\chi_0(T)+3]^2\{2[\chi_0(T)+1]^2+1\}}\ .$$

Comparing formula (1) with the expression (6a) gives the following for $\vec{B}_{\mathrm{ext}}\parallel\vec{B}_{\mathrm{EXT}}$:

$$^{M}\chi_0(T)=\alpha(T)\Pi(T),\quad \frac{\Delta^{M}\chi}{B_{\mathrm{EXT}}^2}=\beta(T)\,^{M}S(T)\ . \tag{9}$$

From formulas (6a) and (6b) it may be seen that for the case where $\vec{B}_{\mathrm{EXT}}\perp\vec{B}_{\mathrm{ext}}$, the value of $\Delta\chi/B_{\mathrm{EXT}}^2$ is one-third of that for $\vec{B}_{\mathrm{EXT}}\parallel\vec{B}_{\mathrm{ext}}$, which is in agreement with experiment (Fig. 3). Hence from temperature measurements $^{M}\chi(T)$ and $\Delta\,^{M}\chi/B_{\mathrm{EXT}}^2(T)$ we may obtain the temperature dependence of the coefficients $\Pi(T)$ and $^{M}S(T)$ (Fig. 7). In this way a pair of equations [formulas (7a) and (7b)] in μ and N is obtained for every temperature value, and the solution of these equations enables the temperature functions $\mu(T)$ and $N(T)$ to be determined. Figure 8 shows on a log-log scale the values of mean magnetic moment μ of the fluctuation and also the mean number N of such ordered regions in the mole substance for various temperatures in the pretransition region. With a reduction in temperature, the value of μ rises from 240 μ_B at a temperature of about 20 K above T_c to 6000 μ_B at a temperature 3 K above T_c, while simultaneously the number N is reduced; consequently, the product μN is weakly dependent on temperature.

B. Susceptibility in an external magnetic field

For comparison with the $\chi(T)$ functions obtained experimentally for various external magnetic fields (Figs. 4 and 6) we show (Fig. 9) the temperature functions $\chi(T)$ calculated numerically from formulas (5a) and (5b) (for the case $B_{\text{EXT}}=B$. In order to determine the temperature function $\mu(T)$ and $N(T)$, use was made of measured values of paramagnetic susceptibility χ_0 and NPE. The analytical relations $\mu(T)$ and $N(T)$ were determined by fitting an exponential function of type $A(T-T_c)^B$ to the measurement points using the least squares methods. From Fig. 9 it may be seen that in the case of parallel $\vec{B}$ and $\vec{B}_m$ fields, more distinct maxima occur than for $\vec{B}\perp\vec{B}_m$. The lack of corresponding extrema in the experimental functions for $\vec{B}_{\text{EXT}}\perp\vec{B}_{\text{ext}}$ (Fig. 6) may be associated with reduced accuracy of measurements due to demagnetization effects. It should be noted that Fig. 6 was prepared based on measurements performed for spherical samples. An advantage is that due to symmetry, it is possible to compare results for the two field configurations, but there is also the drawback that as the demagnetization fields are not considered, the functions obtained are smoother than for cylindrical samples. Moreover, in the case of the spherical samples, measurements were made of the relative value of the susceptibility. The demagnetization effects are also responsible for the shifting of the curves shown on Fig. 6 among the temperature axis, relative to those shown on Figs. 4 and 9. The marked rise in susceptibility below T_c (Figs. 4 and 6) is due to the mechanisms associated with the presence of domain structure,[9] which is not taken into account in the numerical calculations with a basis on the Langevin theory.

ACKNOWLEDGMENT

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