Susceptibility of the weak ferromagnets $ErCrO_3$ and $YCrO_3$ near the critical anomaly

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(Received 3 April 1980)

To investigate the nature of the magnetic properties of canted antiferromagnets in $ErCrO_3$ and $YCrO_3$, ac measurements have been made of the magnetic susceptibility as a function of temperature in the vicinity of T_N using weak magnetic fields less than 1.5 Oe and frequencies from 10 Hz to 100 kHz. The sharp peak in perpendicular susceptibility $\chi_\perp$ was successfully observed and measured at T_N and found to exhibit a dependence on dc magnetic field which is well described by thermodynamic theory of magnetic phase transition in a weak ferromagnet. As a function of a magnetic field H the value of the susceptibility at the peak varies with a $H^{-2/3}$ power law. Below T_N where magnetic domain effects are expected, viscous damped wall motion appears to explain the susceptibility behavior versus frequency in $ErCrO_3$ at least for $T \gtrsim 77$ K.

I. INTRODUCTION

Crystals of $ErCrO_3$ and $YCrO_3$ just below the ordering temperature T_N are canted antiferromagnets in which a ferromagnetic component occurs in the crystallographic c direction due to canting of the two antiferromagnetic sublattices which otherwise align along the easy direction parallel to the a axis.[1]

Both compounds have a distorted perovskite (orthorhombic) crystal structure, and each becomes a weak ferromagnet below T_N which equals approximately 133 and 140 K, respectively. That the direction of the ferromagnetic component is along the c axis is due to the antisymmetric exchange interaction between Cr^{3+} spins.

In $ErCrO_3$ the Er^{3+} spins are oriented along the c axis by the effective field exerted by the ordered Cr^{3+} spins.[2] Complex interactions between two kinds of magnetic ions exhibit a variety of magnetic phenomena. Particular interest has arisen regarding the spin-reorientation (SR) transition whereby the spin configuration changes from the weak ferromagnetic phase to the antiferromagnetic phase below T_{SR} ($=9.8$ K).[3,4] Although the properties of this spin reorientation have been extensively investigated in the last ten years,[5–12] only very few reports[13–15] have pointed out that a critical divergence in the magnetic susceptibility $\chi_\perp$, measured perpendicular to the antiferromagnetic a axis, is expected to appear at T_N in weak ferromagnets according to Borovik-Romanov's theory.[16] Among the orthochromites series, an increase in $\chi_\perp$ was observed for $LaCrO_3$ (Ref. 13) and $YCrO_3$.[14] However, the published susceptibility reported for $ErCrO_3$ (Refs. 2 and 7) shows no anomaly at T_N.

The critical divergence of $\chi_\perp$ appears only in the immediate neighborhood of T_N and is very sensitive to an external magnetic field. Therefore, it is important to make measurements using a small magnetic field together with careful temperature control.

With the above considerations in mind, we have undertaken ac susceptibility measurements over a range frequency between 10 Hz and 100 kHz, and using measuring ac fields of only 0.1-Oe peak oriented along the c axis have successfully observed extremely sharp peak anomalies in $\chi_\perp$ of both $ErCrO_3$ and $YCrO_3$. We interpret the observed variation of $\chi_\perp$ on external magnetic field H around T_N within the framework of Landau's phenomenological theory of phase transitions.

At temperatures well below T_N we have observed in $ErCrO_3$ an anomalously large value of the susceptibility, which reflects the contribution of Ising-like Er^{3+} spins. This anomaly decreased monotonically with frequencies higher than 10 kHz. Interpreting this result in terms of domain-wall motion, we have estimated the domain-wall mobility from the frequency dependence of the macroscopic susceptibility down to 77 K.

II. EXPERIMENTAL

Samples are roughly rectangular-shaped single crystals of $ErCrO_3$ ($4\times2\times0.15$ mm^3) and $YCrO_3$ ($2\times2\times0.1$ mm^3) having (110) and (010) faces, respectively, which have been grown by the flux method. The

samples came from the flux melt already in the desired platelet form having one of the sides coincident with the direction of the c axis. The c axis was identified by x-ray Laue back reflection after roughly aligning the platelet using the angular dependence of the spontaneous magnetic moment. Measurements of the ac magnetic susceptibility were made with a measuring ac field of 0.1-Oe peak over a range from 10 Hz to 100 kHz. The inhomogeneity of the ac field over the sample volume was less than 4% according to calculations based on the actual coil arrangement. Helmholtz coils 19 cm in diameter were used to apply an external dc magnetic field. For zero-field measurements a dc current was adjusted to compensate the geomagnetic field (0.3 Oe). A pair of modulation coils was located in the cryostat as closely to the sample holder as possible, and was aligned to be coaxial with the pick-up coil. A pick-up coil of 10 turns was wound directly on the central sections of the sample using fine insulated copper wire. The magnetically induced signals were fed into a Ithaco model 393 lock-in detector in order to measure an in-phase signal which corresponds to magnetic dispersion. The lock-in output signals were plotted on a chart recorder as a function of temperature. The maximum overall sensitivity of the susceptibility measurment was 10^{-2} emu/cm^3.

The temperature was measured with a Scientific Instruments model P 2AB platinum resistance thermometer located close to the sample as a sensor at the bottom of the sample chamber. The resistance thermometer was measured with an Oxford model S72A resistance bridge. In addition, an electrical heater was used to control the rate of temperature sweep. The observed transition-point anomaly was slightly affected by the rate of change in temperature. Therefore, possible differences in temperature between the sensor and the sample were minimized by using a slow rate of about 2 K/h. The temperature reproducibility was better than 0.05 K at temperatures in the vicinity of phase transitions in both crystals.

To calibrate the magnetic field produced by the coil current, we used a Hall element previously calibrated with a NMR gaussmeter. The values of current for fields less than 1 Oe were extrapolated from those for larger fields within a linear characteristic of the Hall probe. We were able to determine absolute values of the magentic susceptibility of $ErCrO_3$ from comparing with previous data of field-induced magnetization due to spin reorientation obtained using the same method described in a previous paper.[12] For $YCrO_3$ which lacks the spin reorientation, only relative values were obtainable. All results measured at frequencies above 10 kHz were not corrected for a demagnetizing field because the reciprocal susceptibility, as shown in Fig. 1, is sufficiently larger than the sample's demagnetizing factor $N=0.23$ estimated from the value of the temperature-independent susceptibility at 10 Hz.

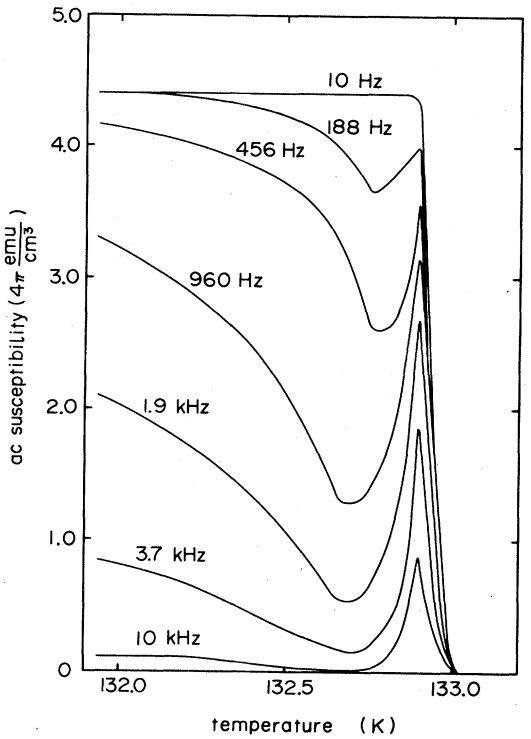

FIG. 1. Temperature dependence of the perpendicular susceptibility $\chi_\perp$ of $ErCrO_3$ around $T_N=132.9$ K. The measuring ac field of the 0.1-Oe peak is parallel to the c axis. Fixed frequencies between 10 Hz and 10 kHz are utilized as indicated.

III. RESULTS

Measurements of the ac magnetic susceptibility $\chi_\perp$ on $ErCrO_3$ were made as a function of temperature in the immediate neighborhood of T_N. The results are shown in Fig. 1. In addition to the curves for frequencies up to 10 kHz shown in Fig. 1, a number of closely spaced curves (not shown) were measured for frequencies up to 100 kHz. These curves revealed striking features, a series of sharp peaks which are emphasized by increasing the frequency, and anomalously large values for low frequencies in the ordered state which are sensitive to temperature.

In Fig. 2 we present the corresponding result for $YCrO_3$. The sharply peaked anomaly in $\chi_\perp$ is also seen at T_N. With lowering frequency we observed no such anomalous increase in the susceptibility as in $ErCrO_3$ except for increases in width at half maximum on the left-hand side of the peak. The dc measurement for the same crystal shows a similar temperature dependence of the susceptibility.

We have not detected any signal for the measurement of the susceptibility parallel to the a axis, $\chi_\parallel$ even at T_N.

Below T_N the domain-wall motion can contribute to

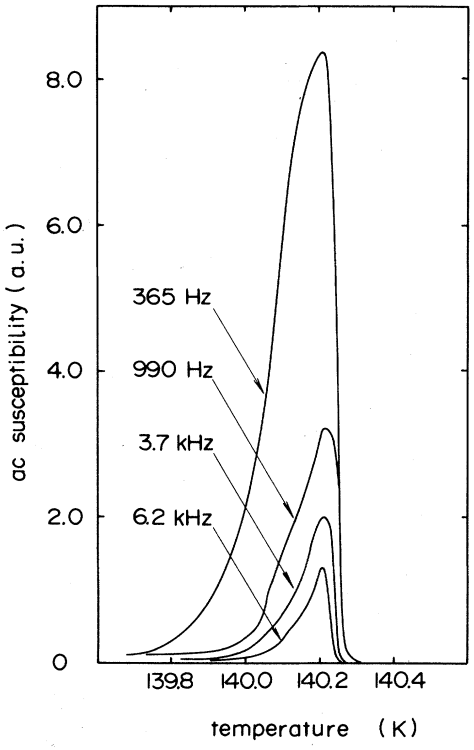

FIG. 2. Temperature dependence of the ac susceptibility of $YCrO_3$ around $T_N = 140.2$ K for several frequencies. The measuring ac field of the 0.1-Oe peak is aligned parallel to the c axis.

the susceptibility as a macroscopic mode in samples which demagnetize into a fine domain pattern. We observed a frequency-dependent macroscopic susceptiblity which may reflect the dynamical character of the domain-wall motion. The results normalized by the value at the low-frequency limit for temperature near T_N, are shown in Fig. 3. The frequency dependence of the macroscopic susceptibility is well described by a monodispersive curve in the neighborhood of T_N as will be discussed.

IV. DISCUSSION

According to the phenomenological thermodynamic theory of weak ferromagnetism,[17] the free energy of the Cr^{3+} spin systems of an orthochromite may be expanded in terms of the sublattice magnetizations $\vec{M}_1$ and $\vec{M}_2$, or equivalently by $\vec{m} = \vec{M}_1 + \vec{M}_2$ and $\vec{l} = \vec{M}_1 - \vec{M}_2$ near the transition point, as follows:

$$F = \tfrac{1}{2}(Al^2 + Bm^2) + \beta(l_x m_z - l_z m_x) + \tfrac{1}{4}Cl^4 - \vec{m}\cdot\vec{H} \ , \tag{1}$$

where $\vec{H}$ denotes the applied field which includes the measuring ac field superimposed upon a parallel static field. Here we have neglected the small anisotropic term and $m^2 l^2$ term, which are negligible to our problem. From Landau's thermodynamical theory of the second-order phase transition, we assume F varies with temperature near T_N as $A - \beta^2/B = \alpha(T - T_N)$ with $\alpha > 0$. The expressions for the magnetic suscep-

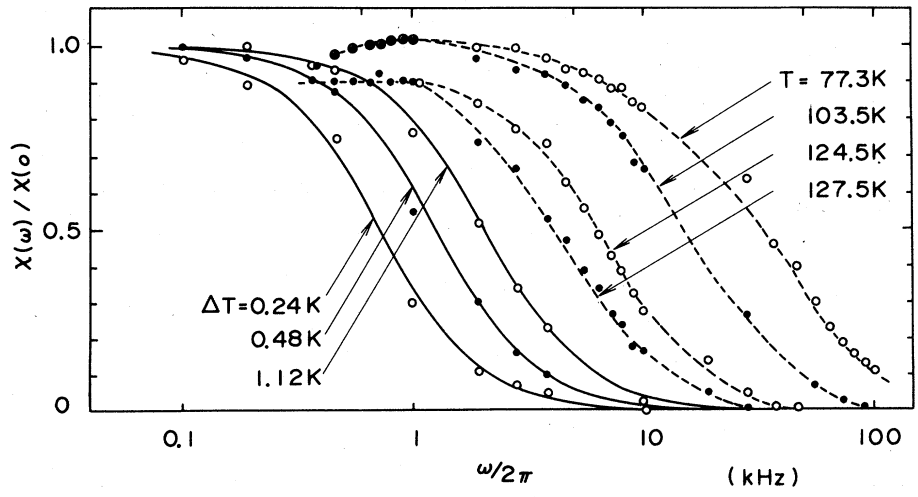

FIG. 3. Frequency dependence of the normalized magnetic susceptibility of $ErCrO_3$ around $T_N = 132.9$ K. The measuring ac field is along the c axis in a frequency from 100 Hz to 100 kHz. The reduced temperature ΔT means $T - T_N$. Full curves indicate a fit to $\mathrm{Re}\chi^*(\omega)$ from Eq. (11). Dashed lines serve as guide to the eye.

tibility are obtained as follows:

$$\chi_\perp \equiv \frac{\partial m_z}{\partial H_z} = \begin{cases} \frac{1}{B} + \frac{\beta^2}{B^2}\frac{1}{\alpha(T-T_N)}, & \text{for } T > T_N \quad (2) \\ \frac{1}{B} + \frac{\beta^2}{2B^2}\frac{1}{\alpha(T_N-T)}, & \text{for } T < T_N \quad , \quad (3) \end{cases}$$

and

$$\chi_\parallel \equiv \frac{\partial m_x}{\partial H_x} = \frac{1}{B} \quad . \quad (4)$$

where $\chi_\perp$ and $\chi_\parallel$ correspond to the susceptibility along the c and a axis in the orthorhombic structure, respectively.

The observed sharp maxima of $\chi_\perp$ common to both $ErCrO_3$ and $YCrO_3$ are a direct consequence of the second term in Eqs. (2) and (3). The sensitivity of the equipment is too small to see the first term. Actually we have detected no signal for the measurement of $\chi_\parallel$ in which no increase at T_N is predicted from Eq. (4). Taking into account the applicability of the approximation used, we obtain the limitation on the closeness to T_N. The temperature interval near T_N for which the expression in Eqs. (2), (3), and (4) is to be satisfied, for not very strong field H, is given by

$$\Delta T \simeq \left(\frac{\beta}{B}\right)^{2/3} \frac{C^{1/2}}{\alpha} H^{2/3} \quad . \quad (5)$$

For $|T-T_N| \lesssim \Delta T$, the expression for $\chi_\perp$ is modified by nonlinear-in-H terms which leave finite values at T_N and lead to the field dependence. Equations (2) and (3) predict that the slope of $\chi_\perp$ vs $(T-T_N)^{-1}$ below T_N is twice as steep as that above T_N. The temperature dependence of the reciprocal susceptibility of frequencies 18.5, 27.4, and 99.4 kHz on $ErCrO_3$ is shown in Fig. 4. The plots for $T < T_N$ and those for $T > T_N$ multiplied by two are nearly aligned in the same straight line for each frequency, in accordance with the theory except for the immediate vicinity of T_N where nonlinear terms become prominent. From this result, we can estimate $\Delta T \simeq 0.03$ K for $H = 0.1$ Oe.

Next, we investigated the effect of applied dc magnetic fields on the critical divergence. According to results in Figs. 1 and 2, the susceptibility in the temperature region of the divergence does not seem to be affected by the macroscopic mode presumably caused by magnetic domain-wall motion at frequencies higher than 10 kHz. The peak susceptibility values at T_N have been plotted against applied fields on a log-log scale in Fig. 5. The results for 27.4 kHz on $ErCrO_3$, and for 27.5 and 89.2 kHz on $YCrO_3$ lie along the straight lines representing $\chi_\perp \propto H^{-2/3}$. It is evident that a nonlinear susceptibility is well described with a $H^{-2/3}$ power law as a function of an applied field.

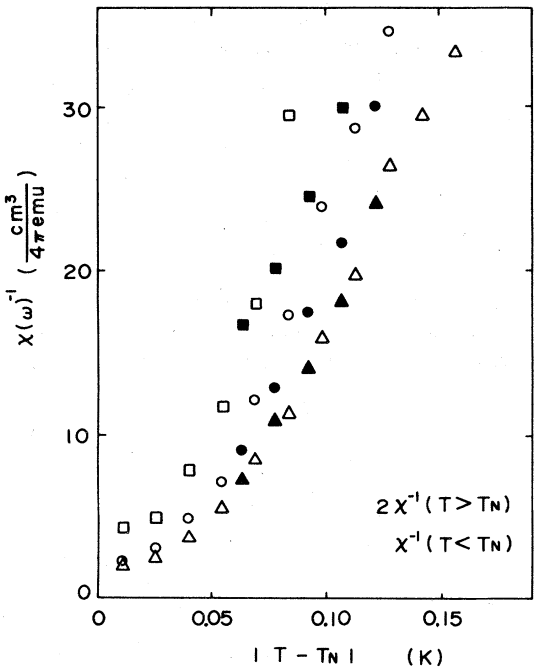

FIG. 4. Temperature dependence of the reciprocal susceptibility in the immediate neighborhood of T_N for $ErCrO_3$. The measuring frequencies are 18.5 kHz (Δ), 27.4 kHz (○) and 99.4 kHz (□) below T_N. Above T_N, the values of the reciprocal susceptibilty are duplicated and the frequencies are corresponding data indicated by solid points.

At $T = T_N$, a field-dependent susceptibility obtained from the free energy of Eq. (1) is given by

$$\chi_\perp (T = T_N) = \frac{1}{3}\left(\frac{\beta^4}{B^4 C}\right)^{1/3} H_z^{-2/3} + \frac{1}{B} \quad . \quad (6)$$

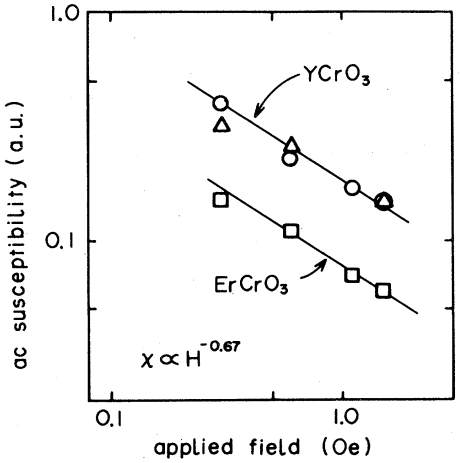

FIG. 5. Dependence of the susceptibility at T_N on an applied field for $ErCrO_3$ at 89.2 kHz (□), and for $YCrO_3$ at 27.5 kHz (○), and 89.2 kHz (Δ). Straight lines indicate a fit to $\chi \propto H^{-2/3}$.

Good qualitative agreement is found between the experimental field dependence on $\chi_\perp$ at T_N and Eq. (6).

Below T_N the anomalously large values of the ac susceptibility in $ErCrO_3$ decreased when the measurements were made with an applied dc field or with the use of higher frequencies. These facts suggest that the anomaly is at least partly due to the domain-wall motion. Any contribution to susceptibility from a macroscopic mode such as domain-wall motion must be much smaller for weak ferromagnets than for pure ferromagnets because of a smaller resultant magnetization. But this is not the case for $ErCrO_3$. The macroscopic mode is enhanced by the Er^{3+} spins which are polarized along the c axis by a molecular fields from ordered Cr^{3+} spins.

We assume a simple model of a 180° wall to explain the relation between the macroscopic susceptibility and the domain-wall motion. As viscous damping applies in weak ferromagnets, the wall mass is negligible.[18] The ac motion of the wall is described by the familiar equation for damped oscillatory motion

$$\beta\frac{dx}{dt}+\alpha x=2M_s h(\omega) \ , \tag{7}$$

where x represents small displacements of the wall from demagnetized equilibrium, M_s the resultant magnetization in a weak ferromagnet, $h(\omega)=h\times\exp(i\omega t)$ the measuring ac field of frequency ω, α the restoring force constant, and β the viscous damping factor. The corresponding equation for the total magnetization is

$$\beta\frac{dM(\omega)}{dt}+\alpha M(\omega)=4M_s^2A[h(\omega)-NM(\omega)] \ , \tag{8}$$

where A is a total area of the cross section of the wall per unit volume and N is the demagnetizing constant. Introducing the shape-dependent restoring force parameter $\alpha'=\alpha+4M_s^2AN$, we have

$$M(\omega)=M_0'\left[1+\left(\frac{\omega}{\omega_c'}\right)^2\right]^{-1/2}\exp[i(\omega t-\phi)] \ , \tag{9}$$

where $M_0'=(4M_s^2Ah)/\alpha'$ is the low-frequency limit of $M(\omega)$ and $\omega_c'=\alpha'/\beta$ is the relaxation frequency. The response of the magnetization lags the field by the angle $\phi=\tan^{-1}(\omega/\omega_c')$. The mobility μ, defined in the usual way as the slope of the wall velocity versus the amplitude of a measuring field curve, is given by

$$\mu=\frac{2M_s}{\beta}=\frac{M_0'\omega_c'}{2M_sAh} \ . \tag{10}$$

Introducing the complex expression in the form of $\chi^*(\omega)$ for the macroscopic susceptibility, we obtain

$$\chi^*(\omega)=\chi_0'\left[1+\left(\frac{\omega}{\omega_c'}\right)^2\right]^{-1/2}\exp(-i\phi) \ , \tag{11}$$

where $\chi_0'=4M_s^2A/\alpha'$ is the low-frequency limit of $\chi^*(\omega)$. The finite sample's susceptibility χ_0' is connected with the corresponding shape-independent susceptibility $\chi_0=4M_s^2A/\alpha$ by the relation $(\chi_0')^{-1}=(\chi_0)^{-1}+N$. At the low-frequency limit, the displacement of the domain wall compensates the measuring field by demagnetization: $\chi_0'\simeq N^{-1}\simeq M_0'/h$. Therefore, from Eq. (10) the mobility is rewritten in the convenient form

$$\mu=\frac{\omega_c'}{2M_sAN} \ . \tag{12}$$

The typical results for $ErCrO_3$ of the frequency dependence of $\mathrm{Re}\chi^*(\omega)$ near T_N are shown in Fig. 3. In the vicinity of the critical temperature the curves are well described by Eq. (11) with $N=0.23$. As temperature is decreased from T_N, despite the curve's deviations from the monodispersive form, the relaxation frequency increases more than ten times.

Let us now estimate the value of the mobility from Eq. (12) assuming a striped domain structure having domain width δ. The wall area parameter A may roughly then be approximated according to $A\simeq\delta^{-1}$. We adopt $\delta\simeq5\times10^{-3}$ cm as suggested by photographs of the domain structure in $DyFeO_3$ (Ref. 19) and $TmFeO_3$.[20] The other numerical values are $M_s\simeq0.2\mu_B$, $N=(4\pi)0.23$, and $\omega_c'=(2\pi)2\times10^4$ at 77 K where ω_c' is determined from $\mathrm{Re}\chi^*(\omega)/\chi_0'=\frac{1}{2}$ in Fig. 3. We find for $ErCrO_3$ at 77 K

$$\mu\simeq2\ \mathrm{cm\,sec^{-1}\,Oe^{-1}} \ .$$

Not enough is known at this point to attempt to determine the precise value of mobility, because it is impossible to determine the domain-structure-dependent parameter A for the sample which was not treated in such a way that an individual domain-wall motion can be studied. The domain structure in orthochromites has not yet been observed. This matter is one of the present questions pending.

V. CONCLUSIONS

In the preceding section we have discussed the frequency and the field dependences of the magnetic susceptibility as a function of temperature in the weak ferromagnets, $ErCrO_3$ and $YCrO_3$, around T_N. Our most interesting result is the observation of divergence in the perpendicular susceptibility at T_N that is expected from the existing theory. For $ErCrO_3$, we have, for the first time, bared the sharp peak in the magnetic susceptibility, which is buried under the contribution from Er^{3+} spin systems, by

the ac method. This crystal is distinguished from others in that it contains two kinds of magnetic ions and they interact with each other. The susceptibility at T_N varies very closely with a $H^{-2/3}$ power law as a function of the applied field H.

In $ErCrO_3$, the mobility of the domain wall is estimated to be 2 cm sec^{-1} Oe^{-1} at 77 K, from the frequency dependence of the macroscopic susceptibility.

ACKNOWLEDGMENTS

The authors wish to express their thanks to the members of our research group for a number of helpful discussions, and would also like to thank A. Ohno for assistance with some of the experiments and to Dr. S. Washimiya for critical reading of the manuscript.

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