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Critical behavior of thermal diffusivity and thermal conductivity of Cr_2O_3 at the Néel transition

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The photopyroelectric technique has been used to study the critical behavior of thermal diffusivity and thermal conductivity of Cr_2O_3 at the antiferromagnetic-paramagnetic phase transition. Deviation from the conventional Van Hove theory has been observed and the results have been explained in terms of a uniaxial model ($n=1$) with energy conservation and a nonconserved order parameter. A sharp dip, due to critical slowing down, is present in the thermal diffusivity while the thermal conductivity shows no anomaly in the critical region. A power-law fit with a background contribution and a term to correct for the thermal-diffusivity anomaly gives a critical exponent $b=-0.09\pm0.02$ and a critical amplitude ratio of $U^+/U^-=0.51$.

The renormalization-group (RG) approach has been widely applied in the last twenty years to the study of both static and dynamic critical phenomena associated with thermal parameters. While in the case of the specific heat, theoretical predictions following the universality hypothesis can be in most cases successfully compared with the very many high-resolution data reported in the literature, the situation is completely different in the case of dynamic quantities such as the thermal diffusivity (D) and thermal conductivity (k). Apart from the case of the superfluid transition of liquid helium, whose critical behavior of thermal conductivity has been extensively studied,[1] there are few high-resolution experimental results available in the literature. This is essentially due to some experimental difficulties in the experimental set-up for high-resolution measurements of thermal-transport properties[2] and also to the sample quality. But even in the case in which these difficulties can be, at least, partially overcome, it could be very difficult to discriminate among different critical behaviors because of the very small difference in the corresponding dynamic exponents. In the case of a magnetic transition in a uniaxial system, for example, the RG calculations have been carried out for two different cases:[3] model A where the order parameter and the energy are not conserved and model C where the energy is conserved while the order parameter is not. The deviation from the dynamic exponent expected from the conventional Van Hove theory[4] are in these cases of the order of $\eta\sim0.02$ and $\alpha\sim0.1$, respectively. Moreover in the case of a uniaxial antiferromagnet whose critical dynamics should be described by model C,[3] it sometimes happens that model A can be more appropriate since the rate of energy transfer from the spins to the phonons and therefore the energy conservation of the spin system, depends on the thermal conductivity of the phonon system. This parameter can often be very large if compared with thermal conductivity of the spin system, thus making the thermal relaxation rate much greater than the order parameter one. The occurrence of crossover in the critical dynamic of many physical systems is therefore possible thus making the comparison between experimental data and theoretical predictions very difficult. Finally we would like to mention that correction terms, as in the case of liquid He, are sometimes necessary to account for the departure from universality.[5]

In this paper we report on the dynamic critical behavior of thermal diffusivity and thermal conductivity at a second-order magnetic phase transition. We have studied the antiferromagnetic-paramagnetic transition of the uniaxial antiferromagnet Cr_2O_3 and deviations from the predictions of the conventional theory have been observed close to the Néel temperature of about 308 K. In particular the results, showing a critical slowing down in D and no anomalies in k strongly support the predictions of the above mentioned model C when correction terms are included in the fitting function.

In Cr_2O_3 the ratio of the anisotropy field to the exchange field ($\sim10^{-4}$) is unusually small for an antiferromagnet and thus the system should be expected to follow a Heisenberg ($n=3$) behavior and perhaps an Ising one ($n=1$) close to T_c. Very little is known about the critical exponent and the available results are contradictory. Staggered magnetic susceptibility measurements[6] show a divergence at the Néel temperature with $\gamma=-1.35\pm0.05$ which is consistent with the predictions of the Heisenberg model, while sound velocity attenuation results[7] yielded $\alpha=0.14$ not too far from what is expected from Ising-like behavior. The specific heat critical exponent has also been measured with a calorimetric technique[8] and the obtained exponent was $\alpha=-0.12$. Although this seems in agreement with what is predicted by the Heisenberg model, the authors, on the basis of a detailed statistical analysis of their data, argue that this conclusion cannot be either confirmed or excluded. One possible explanation for such contradictory conclusions could be, in our opinion, the poor resolution of at least the first two of the above mentioned experiments where

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about 10 data points have been used in the fitting routine to calculate the critical exponents. Regarding the results of Ref. 8 we believe they were probably obtained using a sample which was less pure than the one used in the present experiment as will be discussed later on. We have used a standard photopyroelectric configuration[9] for our measurements which allows the simultaneous determination of the specific heat, thermal conductivity, and thermal diffusivity. Several Cr_2O_3 slices of about 5 mm in diameter and different thickness have been cut and polished from a $3N$ purity single crystal ingot. One side of the sample was in thermal contact with a 300-μm thick $LiTaO_3$ pyroelectric transducer while the other one was heated by a acousto optically modulated 1 mW He-Ne laser, whose light was spread all over the sample surface. The photopyroelectric signal amplitude and phase were recorded by a two phase lock-in amplifier. The sample and the transducer were contained in a oven whose temperature rate change was of (4 ± 1)mK/min. Data were collected every 2 mK and the sample temperature was controlled by means of a thermistor. The sample surfaces have been blackened with a carbon layer to make sure that no contribution due to possible reflectivity changes are present in the signal. A test sample with a thermally thin carbon layer of the same thickness deposited on a glass was used to check the opacity of the coating.

Figure 1 shows the behavior of D in the vicinity of the Néel temperature. A sharp dip to the critical slowing down is clearly evident. The data analysis is based on the assumption that the diffusivity data can be described by a regular term plus a singular one,

$$D=D_{\rm sing}+D_{\rm reg}=U^{\pm}|t|^{-b}+Wt+V\ , \qquad (1)$$

where U^+ and U^- are the critical amplitudes for $T>T_c$ and $T<T_c$, respectively, b is the critical exponent. The data have been fitted by a nonlinear fitting routine with each point weighted with an uncertainty of 0.04%. Data that, from a preliminary analysis, seem to be affected by rounding were excluded. Next we fix T_c and all the other parameters were least-squares adjusted. T_c was then released and the data fitted again. Finally $t_{\max}$ and $t_{\min}$ were varied to have the widest temperature range where the data could be fitted by a single power law. The quality of the fit was estimated not only from the rms deviation but also from the deviation plot.

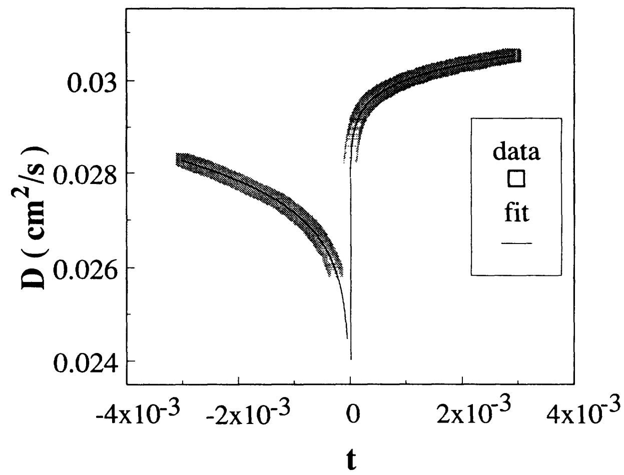

FIG. 1. Thermal diffusivity of Cr_2O_3 near the Néel temperature as a function of the reduced temperature $t=(T-T_c)/T_c$. The used symbols are much greater than the experimental errors (see text). The solid curve represents fit 4 of Table I.

The results of the fit are reported in Table I. The value $b=-0.20$ we obtained in fit 1 using Eq. (1) does not agree with any of the theoretical predictions for the critical behavior of D in uniaxial systems. We, in fact, expect[3] for model A $z=2+c\eta$ [where $c=0.726(1-1.69\varepsilon+\cdots)$] and, from the scaling law $z=2-b/\nu$,[10] we obtain $b\sim-0.015$ while for model C $z=2+\alpha/\nu$ and $-b=\alpha=0.115$. The disagreement is even more striking if we consider an anisotropic antiferromagnet, where $z=\frac{3}{2}$ and $b\sim-0.35$. This seems to suggest a nonuniversal critical behavior for Cr_2O_3. On the other hand, the rms value of fit 1 is larger than all the others reported in Table I, thus indicating a poor fit quality. We next tried to allow a discontinuity in the background term at T_c ($V\neq V'$). It should be noted that discontinuity in thermal diffusivity has been reported in the literature for several liquid crystal phase transitions

TABLE I. Results of fitting for the data. Fit 1 has been obtained using Eq. (1), while in fits 2 and 5 $V^-\neq V^+$. Results of fits 3 and 4 have been obtained by including a correction term (see text).

	Fit 1	Fit 2	Fit 3	Fit 4	Fit 5
$t_{\max}$	8×10^{-3}	8×10^{-3}	8×10^{-3}	3×10^{-3}	3×10^{-3}
$t_{\min}$ $(T<T_c)$	1.6×10^{-5}	2×10^{-4}	1.8×10^{-4}	2.5×10^{-4}	3×10^{-4}
$t_{\min}$ $(T>T_c)$	4.5×10^{-4}	3.5×10^{-4}	3.8×10^{-4}	2×10^{-5}	2×10^{-5}
T_c [K]	307.14 ± 0.02	307.176 ± 0.015	307.190 ± 0.015	307.240 ± 0.015	307.254 ± 0.015
b	-0.20 ± 0.03	-0.27 ± 0.03	-0.015 ± 0.002	-0.09 ± 0.02	-0.09 ± 0.02
U^- [cm^2/s]	$(2.8\pm0.5)\times10^{-3}$	$(3.3\pm0.6)\times10^{-3}$	$(2.47\pm0.2)\times10^{-2}$	$(6.5\pm0.3)\times10^{-3}$	$(1.3\pm0.1)\times10^{-2}$
U^+ [cm^2/s]	$(6.1\pm0.5)\times10^{-3}$	$(3.5\pm0.4)\times10^{-3}$	$(2.76\pm0.2)\times10^{-2}$	$(1.27\pm0.04)\times10^{-2}$	$(5.6\pm1.0)\times10^{-3}$
W [cm^2/s]	$(-6.1\pm0.6)\times10^{-4}$	$(-3.5\pm0.8)\times10^{-4}$	$(-2.8\pm1.5)\times10^{-4}$	$(2.4\pm0.5)\times10^{-3}$	$(3.5\pm2.5)\times10^{-5}$
V^- [cm^2/s]	$(2.50\pm0.05)\times10^{-2}$	$(2.48\pm0.06)\times10^{-2}$	$(2.35\pm0.01)\times10^{-3}$	$(2.02\pm0.05)\times10^{-2}$	$(1.58\pm0.01)\times10^{-2}$
V^+ [cm^2/s]	$(2.50\pm0.05)\times10^{-2}$	$(2.74\pm0.04)\times10^{-2}$	$(2.35\pm0.01)\times10^{-3}$	$(2.02\pm0.05)\times10^{-2}$	$(2.54\pm0.01)\times10^{-2}$
F^-			$(4.8\pm0.5)\times10^{-2}$	$(6\pm1)\times10^{-1}$	
F^+			$(3.0\pm0.5)\times10^{-2}$	$(-3.7\pm0.3)\times10^{-1}$	
U^+/U^-	2.18 ± 0.57	1.06 ± 0.31	1.12 ± 0.17	0.51 ± 0.08	0.43 ± 0.11
rms	0.001 64	0.000 50	0.000 44	0.000 44	0.000 51

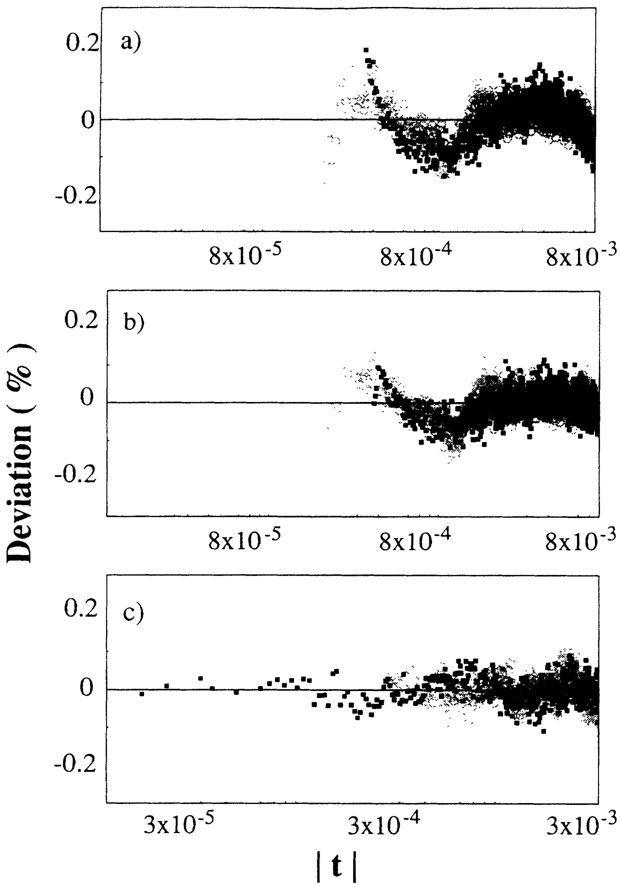

FIG. 2. Percentage deviation of the thermal diffusivity data (■ for $T > T_c$ and ○ for $T < T_c$) from the best fits: curves a, b, and c, correspond to fits 2, 3, and 4, respectively, of Table I.

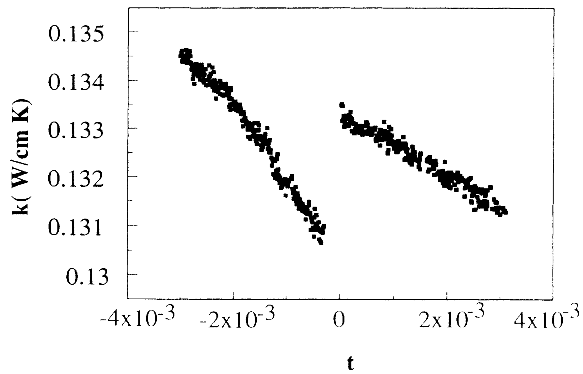

FIG. 3. Thermal conductivity of Cr_2O_3 near the Néel temperature as a function of the reduced temperature $t=(T-T_c)/T_c$.

and no explanation is, until now, available.[11] Even if the fit quality improved, as shown from the comparison of fits 1 and 2 rms values, we obtained $b=-0.27$ which again does not agree with any theoretical prediction. Moreover, systematic deviations are clearly evident in the corresponding deviation plot reported in Fig. 2(a). As mentioned earlier on, a correction term can sometimes be needed in critical dynamic.[5] We used a correction to scaling factor to the first order in ε expansion $(1+F^{\pm}|t|^{x})$ similar to the ones usually used in the description of the critical behavior of specific heat. The exponent $x \sim 0.5$, derived from static corrections, is the same as the one for the specific heat.[12] The obtained results correspond to fit 3, the deviation plot is shown in Fig. 2(b). Both the rms value and the deviation plot demonstrate as in this case the quality of the fit has improved, even if small deviations, comparable with the experimental total error, are still present. The exponent $b=-0.015$, however, is again not in agreement with any theoretical prediction. Since, as stated earlier on, there is a possibility of a crossover for this material from Heisenberg to Ising very close to T_c, we tried to reduce t_{max}, using the same function of fit 3. The obtained results correspond to fit 4 of Table I, the corresponding deviation plot being shown in Fig. 2(c) and the fit curve is the solid line in Fig. 1. The fit has greatly improved as can be seen from the rms value and from the deviation plot. Moreover the value of the exponent $b=-0.09\pm0.02$ is in very good agreement with what is expected from model C. It is possible from our measurements to also calculate the critical exponent of the specific heat, which for model C must be equal to b, and, in the same reduced temperature range of the diffusivity, we obtained $\alpha=(0.10\pm0.02)$ and a amplitude ratio of 0.48 ± 0.03. A detailed analysis of the specific heat results will appear in a forthcoming paper. Also shown in Table I are the results of fit 5, obtained with the same fitting function of fit 2 in the same t range of fit 4. Even if the deviation plot (not shown) is only slightly worse than the one of fit 4, the rms value is larger. This result, together with the results of fits 2 and 3, seems to confirm that the function with the correction term is more suitable to fit the experimental data. It should be noted that our results give a strong indication of an Ising-like behavior even if the anisotropy field is so small with respect to the exchange one. It is well known that the anisotropy field can be also due to the presence of mechanical stresses thus making this field sample dependent. To check for the possible influence of mechanical stresses due to the crystal growth or lattice defects, we annealed our sample at 850 °C for 40 hours in a N_2 atmosphere allowing it to cool down to room temperature in 24 hours. We repeated the measurements and within the experimental errors we obtain the same results for c, k, and D. This makes an increase of the anisotropy field dependent from sample characteristics very unlikely. Regarding the purity of our sample it seems to be larger than the one of Ref. 8 since the critical temperature is about 0.1 K higher.

Figure 3 shows the behavior of the thermal conductivity in the vicinity of the Néel temperature. No anomaly in k has been found in the critical region, thus supporting the above-mentioned results giving equal critical exponents for the specific heat and the thermal diffusivity. A small discontinuity is evident in the critical region, Even if the origin of this discontinuity, which is only about 1.5% and completely contained in the region of rounding of the D and c data, is not very clear, we think that the data strongly suggest the uniaxial critical behavior of Cr_2O_3 in investigated reduced temperature range.

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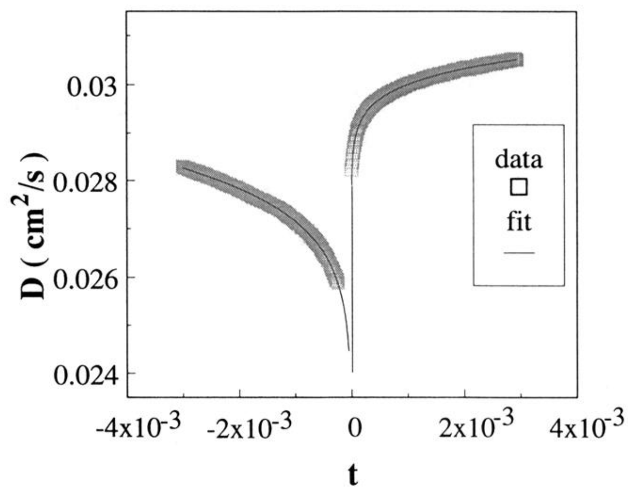

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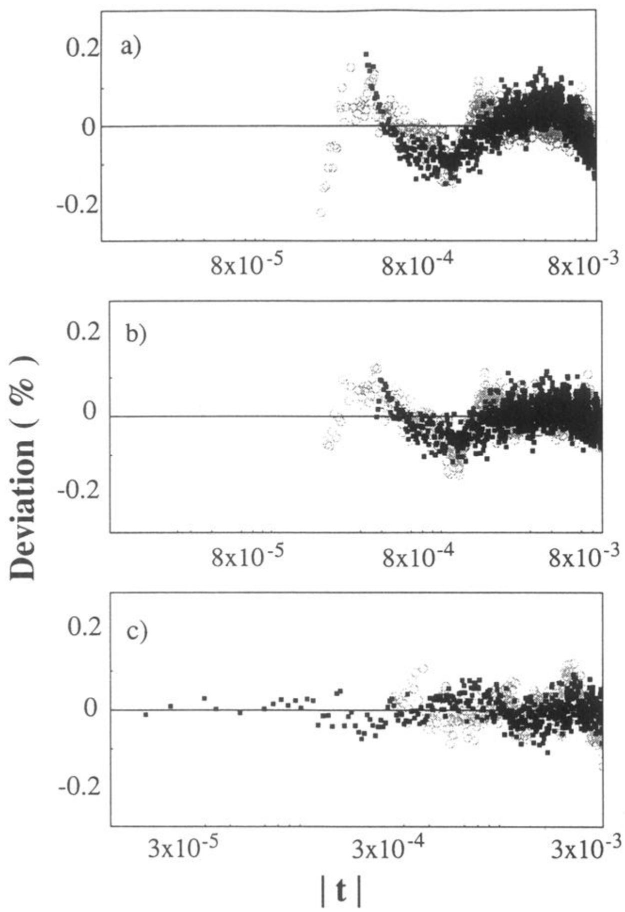

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