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Spin dynamics in the mixed valence alloy $Ce_{1-x}Th_x$

S. M. Shapiro and J. D. Axe
Brookhaven National Laboratory, Upton, New York 11973*

R. J. Birgeneau
Department of Physics, Massachusetts Institute of Technology,† Cambridge, Massachusetts 02139
and Brookhaven National Laboratory, Upton, New York 11973*

J. M. Lawrence‡ and R. D. Parks
Department of Physics and Astronomy, University of Rochester,§ Rochester, New York 14627
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Temperature-dependent neutron-scattering experiments have been performed on a polycrystalline sample of $Ce_{0.74}Th_{0.26}$ which undergoes a first-order γ-α valence transition at $T_V \sim 150$ K. By a measurement of the temperature dependence of the lattice parameter and use of Végard's law, we estimate the temperature behavior of the valence of Ce. The Q dependence of the magnetic scattering is found to follow the form factor of the Ce^{3+} ion surprisingly well. In the inelastic scans, particular attention has been paid to the subtraction of the phonon background via an inelastic study of an identically sized and shaped sample of the nonmagnetic material $La_{0.73}Th_{0.27}$. The corrected $Ce_{0.74}Th_{0.26}$ spectra have then been expressed in the form of the imaginary part of the susceptibility $\chi''(\vec{Q},\omega)$. The γ-phase dynamic susceptibility is a broad feature with significant intensity extending beyond 70.0 meV (the limit of our measurement) with a peak near $\sim$20.0 meV. On cooling below T_V the susceptibility decreases in magnitude and broadens such that the peak is beyond 70.0 meV. These results are compared with the macroscopic magnetic susceptibility which exhibits behavior similar to $\chi(\vec{Q})$ obtained from $\chi''(\vec{Q},\omega)$ by a Kramers-Kronig analysis.

I. INTRODUCTION

Over the past several years there has been considerable interest in materials exhibiting a nonintegral valence.[1-3] This property has been studied mostly in rare earths and their compounds. In many of these materials the rare-earth ion undergoes a change of valence in response to a temperature or pressure variation, or, as a result of alloying. Cerium and the compounds of Ce and Sm have been the most extensively studied. In the Sm mixed-valence systems the atomiclike $4f$ state is usually situated energetically slightly below the $5d$-$6s$ conduction band. As the pressure, temperature, or composition is varied the $5d$-$6s$ bands broaden and move down closer to the $4f$ level and finally, according to current thinking, at some critical value the $4f$ level is pinned at the Fermi level. It is in this latter state that the system is defined as a mixed-valence material.[1] For the Ce systems, the situation is less clear because of the more extended nature of the $4f$ wave functions. A band picture might therefore be more appropriate to describe the Ce ions in both valence states. In such valence transitions, generally no change in crystal symmetry occurs but the lattice parameter usually shows a large contraction as the $4f$ level and conduction band approach each other.[1]

It is well known that pure Ce exists as a face centered cubic (fcc) metal with the cerium atom at least approximately in the Ce^{3+} ($4f^1$) configuration, the so-called γ phase of Ce. As the pressure is raised to ~8 kbars, Ce^{3+} transforms to the collapsed α phase with the same fcc structure but with a 20% smaller volume.[4,5] In this state the valence of the $4f$ level is no longer Ce^{3+} but, in the mixed-valent picture, has become[5] $Ce^{3.67+}$. As the pressure is further increased to ~50 kbars, another transformation occurs to the α' phase[5] and a full electron is given up to the conduction band with the valence now being Ce^{4+}.

The γ to α transition can also be induced with a lowering of temperature after alloying with thorium.[6] Depending upon the thorium concentration the transition of $Ce_{1-x}Th_x$ can be first order, second order, or continuous. Recently, Lawrence *et al.*[7] have studied the critical behavior at the valence instability and have observed mean-field-like behavior. Some recent temperature-dependent diffuse quasielastic-neutron-scattering measurements were performed on $Ce_{0.8}Th_{0.2}$ in order to establish the fractional occupancy of the $4f$ configuration in the α phase.[8] However, as we shall discuss in Sec. IV, there are certain errors in the experimental procedure which vitiate the principal results.

In the present paper, we report an investigation of the inelastic magnetic scattering from $Ce_{1-x}Th_x$ with $x = 0.26$, a concentration very near the critical concentration but just within the first-order re-

gime.[9] The advantage of being near the critical point where a phase transition occurs is that it is possible to study explicitly the dependence of the spin dynamics on the valence of the system. The temperature dependence of this scattering will be presented together with the derived imaginary part of the generalized susceptibility $\chi''(Q,\omega)$. These results will be compared with bulk magnetic susceptibility measurements.[10] Unfortunately, at present, there is no adequate theory for the magnetic behavior of mixed valent materials. Consequently, we present our results with only limited discussion of the theoretical interpretation. However, with the completion of this neutron-scattering study together with the extensive work by Parks, Lawrence, and co-workers[3,7,10] very complete information now exists on the static and dynamic behavior of $Ce_{1-x}Th_x$. It is hoped, therefore, that this detailed information on a model system will provide an appropriate stimulus for a detailed theoretical investigation.

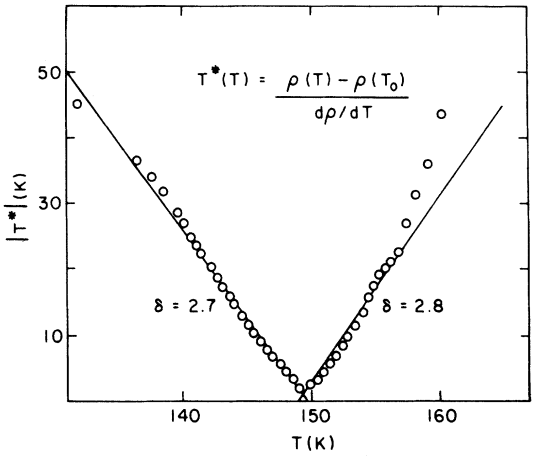

FIG. 1. Plot of $|T^*(T)| = |\Delta\rho/(d\rho/dT)|$ utilizing the resistivity $\Delta\rho = \rho(T) - \rho(T_c)$ of the sample used in the neutron experiment. For $x \simeq x_0$ one expects $\Delta\rho \alpha (T - T_c)^{1/\delta}$ with $\delta = 3$; hence $T^* = \delta(T - T_c)$. This plot exhibits sample quality, inhomogeneities being exhibited as a rounding at the apex. The crossing of the solid lines indicates that the sample is weakly first order (Ref. 7).

II. PRELIMINARY DETAILS

A. Sample preparation and characterization

Polycrystalline samples were prepared by arc melting. The starting materials were: United Mineral and Chemical cerium and lanthanum, quoted as 99.99% overall purity, 99.995% with respect to common metals; and Alfa Ventron thorium, quoted as 99.95% overall purity, 99.98% with respect to common metals. The major impurities were interstitial oxygen and hydrogen. It is well known that even with careful handling of the best commercially available material, the rare earths can contain as much as 1% of these interstitials.

We have had difficulty making large $Ce_{1-x}Th_x$ samples which are highly homogeneous. When the arc size is smaller than the sample size, thermal gradients in the melt promote segregation. To minimize this, we first prepared and homogenized seven 3-g buttons; these were then melted together to form a large ingot. This was machined and then annealed 24 h at 800 K to relieve strains. The same procedure was followed for the $La_{1-x}Th_x$ sample.

As a preliminary test for sample quality we measured the resistivity from 130 to 300 K. Although the sample had nominal concentration $x = 0.269 > x_0 = 0.265$ (x_0 being the nominal critical concentration), in fact the resistivity exhibited a weak first-order discontinuity and comparison of the data with the predictions of the equation of state[10] suggested an effective concentration $x_{eff} = 0.264$. Hence, a small level of segregation and inhomogeneity was certainly present. The effect of this would be serious for very fine scale studies close to the critical point, where the system properties vary rapidly with x and T. However, for the neutron experiment reported here, where temperature increments were fairly large, the sample was quite adequate. Indeed a critical exponent plot (Fig. 1) for the sample exhibits, albeit roughly, the expected exponent behavior over about a decade of reduced temperature above and below T_c.

B. dc magnetic susceptibility

The bulk dc magnetic susceptibility $\chi(T)$ for a separate sample of $Ce_{1-x}Th_x$ with comparable concentration ($x = 0.269$) is shown in Fig. 2,. as well as a plot of $\mu_{eff} = T\chi/C$. Here $C = 5760 \times 10^{-6}$ emu K/g—Ce is the $J = \frac{5}{2}$ free-ion Curie constant. It has been shown elsewhere[10] that (i) in the α state the susceptibility is independent of temperature out to about 50 K. Use of the crude formula $\chi = C/\Gamma$ gives the value $\Gamma = 0.13$ eV. Without attempting to justify the significance of such a formula, we note that Γ seems to be roughly of the order of the α state linewidth reported in Sec. III. (ii) For $250 < T < 350$ K the susceptibility follows $\chi = C'/[T + \theta(x)]$ where C' is within 4% of the free-ion value and $\theta(x)$ for $x = 0.27$ is approximately 150 K (0.012 eV). Reservations about Curie-Weiss behavior over limited regions of data, and about the significance of such a formula, are in order. Nevertheless it is worth noting that the value of θ is of the same order as the width of the neutron line in the γ state, and very close to the value of the phase transition temperature. (iii) Close to

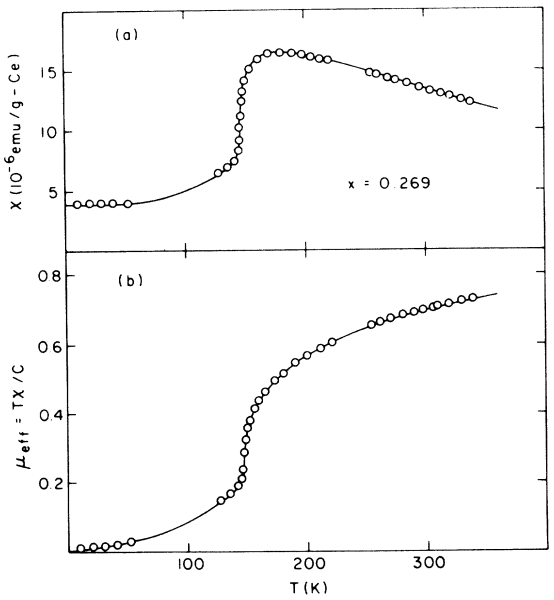

FIG. 2. (a) dc bulk susceptibility $\chi(T)$ for a separate sample of $Ce_{1-x}Th_x$ with $x=0.269$. The low-temperature data have been corrected for a contribution arising from $\sim\frac{1}{2}\%$ untransformed magnetic cerium ions (Ref. 10). (b) The effective moment $\mu_{\rm eff}=T\chi/C$. This should saturate to unity at high temperatures.

T_c critical exponent plots show that $\Delta\mu_{eff}=\mu_{eff}(T)-\mu_{eff}(T_c)\alpha(T-T_c)^{1/\delta}$ with $\delta\simeq 3$, the exponent for the order parameter on the identical thermodynamic pathway. These plots are linear in the interval $[T_0-30\ \text{K}, T_0+30\ \text{K}]$ while similar plots for $\Delta\chi$ or $\Delta[(T+\Sigma)\chi]$ for various choices of Σ show strong curvature already at $T_c\pm 10$ K, and give poor values for δ. Hence, $\Delta\mu_{eff}$ is linearly proportional to the order parameter.

C. Neutron experiments

Two different polycrystalline samples of $Ce_{1-x}Th_x$ with $x\simeq 0.264$ weighing 5 and 21.7 g were used in this study. For obvious reasons most of the data was taken on the larger sample. As noted above, for $x=0.264$ the transition is weakly first order with transition temperatures $T_{V_1}=147.5\pm 0.5$ K and $T_{V_2}=153.5\pm 0.5$ K on cooling and heating, respectively (Fig. 3). The large sample was slablike with dimensions $1.43\times 0.57\times 0.26$ in. A sample of $La_{0.73}Th_{0.27}$ with approximately the same dimensions and weight was also studied in order to estimate the contribution of the nuclear (i.e., phonon) scattering to the total inelastic scattering in the Ce-Th system.

The samples were loosely held in an aluminum can by means of small aluminum straps in order to minimize any stresses applied to the crystal. Helium gas was placed in the aluminum can to increase the heat transfer. The can was then mounted on the cold finger of an Air Products Company closed-cycle Displex System. The temperature could easily be regulated to within ±0.1 K over the temperature range covered, 10–300 K.

The experiments were performed on a triple-axis spectrometer at the Brookhaven High-Flux Beam Reactor. The spectrometer was operated in the constant-Q mode of operation with a fixed analyzer energy and a varying incident energy. This mode of operation is convenient since no corrections to the observed intensities due to changes in the instrumental resolution are needed as the energy varies.[11] The horizontal collimation was $40'-20'-40'-40'$ between the reactor and monochromator, the monochromator and sample, the sample and analyzer, and the analyzer and detector, respectively. To cover the energy range 0–30 meV a pyrolytic graphite (PG) monochromator and analyzer were used with the latter set to analyze 30.0-meV neutrons. For energy transfers greater than 30.0 meV, the (00.2) reflection of beryllium was used as a monochromator with the PG analyzer set for 40.0 meV. The instrumental energy resolution varied between 1.5 and 7 meV for the low- and high-energy ranges, respectively. No filter was used since any higher-order contamination was negligible due to the Maxwellian spectral profile of the reactor.

III. RESULTS

Figure 3 shows our measurement of the lattice parameter of $Ce_{0.74}Th_{0.26}$ between 10 and 300 K as determined from the position of the (111) Bragg peak. A discontinuity is observed near 150 K and, as the inset shows, there is a 6-K hysteresis confirming the first-order nature of the phase transition. The sample was cycled several times through

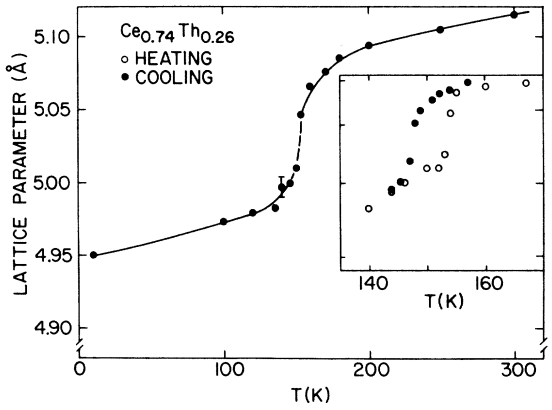

FIG. 3. Lattice parameter of $Ce_{0.74}Th_{0.26}$ as a function of temperature. The inset shows the observed hysteresis in the transition region.

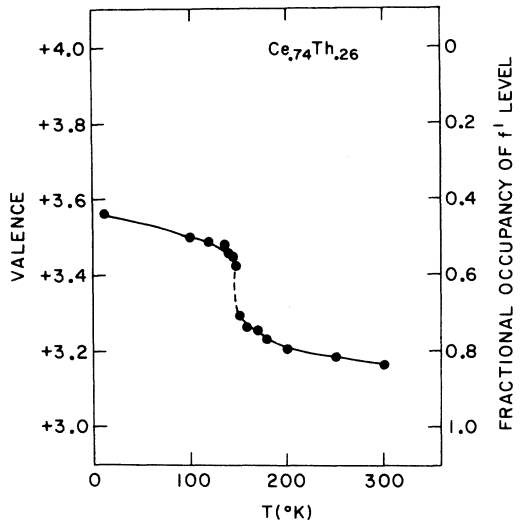

FIG. 4. Valence of Ce and the fractional occupancy of the $4f^1$ level obtained from the lattice parameter measurements.

the transition; the intensity, width, and position of the (111) Bragg peak was always reproduced. There was no evidence for the existence of an intermediate β-Ce phase at any temperature in our experiment.

The simplest method of estimating the valence is from the atomic volume as reflected in the measured lattice parameter. The valence is then deduced by interpolation assuming a linear relation between the ionic radii of the f^n and f^{n-1} configuration.[5] For our measurements on $Ce_{1-x}Th_x$, Végard's law[12] was used to calculate the lattice constant of an equivalent Ce sample, that is,

$$a_{Ce}=\frac{1}{1-x}(a_{Ce_{1-x}Th_x}-xa_{Th}), \qquad (1)$$

where $a_{Th}=5.0741$ Å was used.[13] No correction was made for thermal expansion since this effect is more than an order of magnitude smaller than the contraction due to the valence change as evidenced by the 0.05% contraction of $La_{1-x}Th_x$ sample on cooling from 200 to 100 K. Once the temperature dependence of the lattice parameter of the equivalent Ce was obtained the ionic radius was calculated and the valence interpolated, using the values of $a(Ce^{3+})=5.221$ Å and $a(Ce^{4+})=4.661$ Å.[5] The results of this method are given in Fig. 4. It is inferred that at room temperature the valence in the γ phase is 3.17 and increases to 3.29 just above the transition. At T_c, there is an abrupt jump in the valence to 3.39 just within the α phase and a continuous increase to 3.56 at 10 K. These can be compared with measurements on pure Ce under pressure.[5] For γ cerium at room temperature and atmospheric pressure the valence is ~3.06, while well within the α phase it reaches a value of 3.67.[5] Hence, the valence of Ce in $Ce_{1-x}Th_x$ is similar to that of pure Ce; it should be emphasized, however, that Végard's law is an approximation and the linearity of the ionic radius with valence is an untested assumption, especially in the critical region.

Let us now consider the inelastic measurements. Figure 5(a) shows an energy scan at 250 K of the γ phase $Ce_{0.74}Th_{0.26}$ at $Q=3.0$ Å^{-1} from 0 to 40 meV. This Q was chosen so as not to coincide with any Bragg peak and to be large enough to allow sufficient energy transfer. At 40.0 meV the signal is still well above background, and as seen in Fig. 6, the scattering extends to energies greater than 70.0 meV. In order to deduce information about the spin fluctuations, however, the phonon scattering must first be subtracted from the spectra so that only the magnetic scattering remains. In order to estimate the nuclear contribution to the total intensity, the measurements were repeated

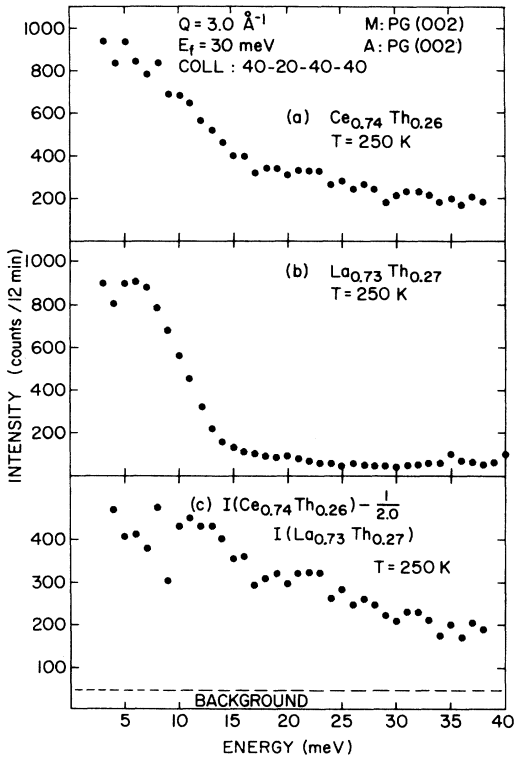

FIG. 5. (a) Inelastic neutron spectra of polycrystalline $Ce_{0.74}Th_{0.26}$ at $Q=3.0$ Å^{-1} and $T=250$ K. (b) Inelastic neutron spectra of $La_{0.73}Th_{0.27}$ at $Q=3.0$ Å^{-1} and $T=250$ K. (c) Difference between (a) and (b). The $La_{0.73}Th_{0.27}$ is divided by 2.0 to account for the different scattering amplitude of Ce and Th. This yields the magnetic scattering from Ce atoms.

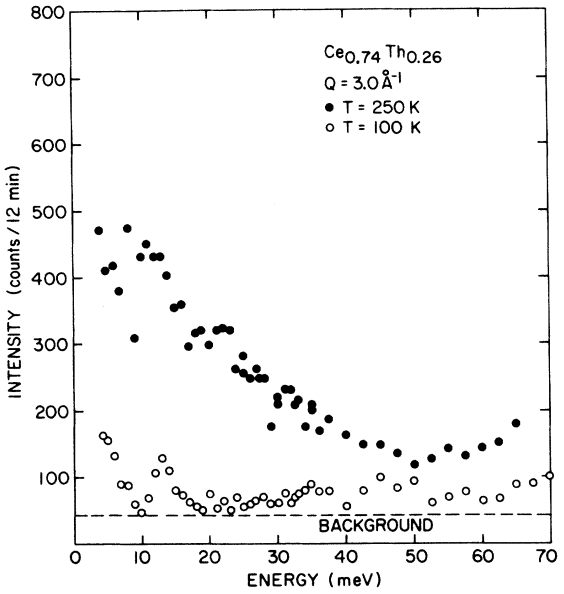

FIG. 6. Inelastic magnetic scattering spectra from 4 to 70 meV in the γ phase (T = 250 K) and α phase (100 K) of $Ce_{0.74}Th_{0.26}$.

on an almost identical size sample of $La_{0.73}Th_{0.27}$. This spectrum is shown in Fig. 5(b). Since the La is nonmagnetic all of the observed scattering is nuclear in origin. For large Q the measured profile approximates the phonon density of states weighted by the phonon structure factors. Significant phonon scattering is observed up to 15.0 meV. In order to extract the magnetic scattering for $Ce_{0.74}Th_{0.26}$ we assume that the phonons in fcc $La_{0.73}Th_{0.27}$ are closely similar to those in fcc $Ce_{0.74}Th_{0.26}$. Dividing the intensity of $La_{0.73}Th_{0.27}$ spectra by 2.0, which takes into account the different scattering amplitudes of Ce and La, we then perform a point-by-point subtraction of the data and arrive at the spectrum of the magnetic scattering from $Ce_{0.74}Th_{0.26}$ shown in Fig. 5(c). The background has been determined by the intensity of the $La_{0.73}Th_{0.27}$ sample at energies $\hbar\omega > 30.0$ meV, well above the phonon cutoff frequency. For $Q = 3.0$ Å^{-1}, about half of the observed signal at $\hbar\omega \sim 10$ meV is nuclear in origin; thus the resultant line shape for the corrected magnetic spectrum [Fig. 5(c)] is quite different from the observed spectrum [Fig. 5(a)]. We can estimate that the subtraction procedure is adequate to ~25%. This uncertainty is due to the differences in absorption lengths of La and Ce and the effects of multiple scattering which are not included in the factor 1/2.0.

The assumption that the phonon density of states in $La_{0.73}Th_{0.27}$ is closely similar to that of $Ce_{0.74}Th_{0.26}$ is undoubtedly valid for the γ phase since the atomic sizes, masses and valence of Ce and La are nearly identical. This may not be the case as the temperature of $Ce_{0.74}Th_{0.26}$ is reduced and the valence starts to change. Indeed, it is expected that the lattice vibration energies will change somewhat as a result of the valence transition[14,15] although this effect should be small on the scale of energies relevant here. Unfortunately, we have no completely independent method of assessing possible errors at lower temperatures; we might note, however, that specific-heat measurements on pure α-Ce at low temperatures provide a Debye energy of 15.4 meV,[16] a value in agreement with the observed cutoff for phonons in $La_{0.73}Th_{0.27}$. Thus, although the shape of the density of states may vary due to the valence instability, the cutoff frequency is nearly constant and, at the minimum, the subtraction procedure is certainly valid for energies $\hbar\omega > 15.0$ meV. This can be verified by setting the spectrometer for a given energy transfer above the phonon cutoff and varying the scattering angle or momentum transfer. Results for $\hbar\omega = 30$ meV are shown in Fig. 7 for γ phase $Ce_{0.74}Th_{0.26}$ just above T_{V_1}. The background was determined with our lanthanum sample and has been already subtracted in the figure. The scattering falls off smoothly as a function of Q which is characteristic of a magnetic form factor behavior. Measurements were also extended down to 0.3 Å^{-1} at $\hbar\omega = 4$ meV with no anomaly observed.

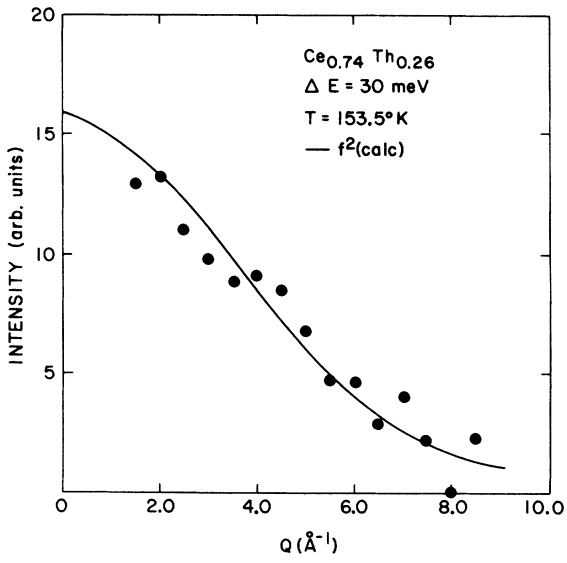

FIG. 7. Q dependence of magnetic scattering from $Ce_{0.74}Th_{0.26}$. This spectra was taken at a constant transfer of 30.0 meV at T = 153.5 K, just before the transition to the α phase. The background was subtracted from a similar scan with $La_{0.73}Th_{0.27}$ sample. The solid line is a fit with the form factor calculated in Ref. 19.

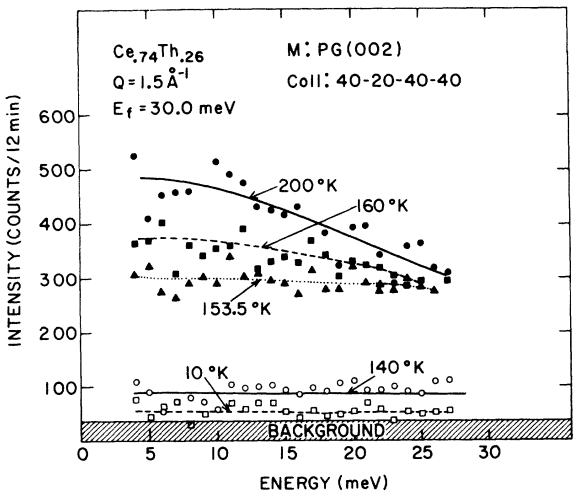

FIG. 8. Temperature dependence of low-energy spectra of $Ce_{0.74}Th_{0.26}$. The lines are drawn as guides to the eye. For $\Delta E < 16.0$ meV the phonon contribution has already been subtracted.

There are, in addition, several internal consistency checks. Firstly, we have carried out this phonon subtraction procedure at both $Q = 1.5$ and 3.0 Å^{-1}. The relative intensities of the phonon and magnetic scattering vary by a factor of three in going from one wave vector to the other. Nevertheless, the residual magnetic scatterings so deduced at the two wave vectors are identical to within a simple scale factor which, as we shall show below, is consistent with the square of the $4f^1$ form factor. Secondly, the phonon intensity varies smoothly with temperature according to the boson population factor while the residual scattering changes drastically around 150 K. Thus any serious error in the phonon subtraction procedure may reflect itself in irregular residual spectra around 10 meV especially below T_c. In fact, the corrected spectra after subtraction are continuous at all temperatures and show no large systematic variations. We are confident, therefore, that our $La_{0.74}Th_{0.26}$ phonon subtraction procedure is adequate. It is important to emphasize that errors in the subtraction procedure only affect the data in the energy range of 4–15.0 meV. As we shall see, the important physics lies in the energy range beyond 15.0 meV and the results arrived at below will be unaffected by the subtraction. We should emphasize in turn that erroneous conclusions would be obtained if the phonon part of the spectra were ignored.

Having subtracted the phonon contribution from the inelastic scattering and demonstrating that the remainder is magnetic in origin we now describe its temperature dependence. Figure 8 shows the low-energy spectra (0–27 meV) of the magnetic scattering at $Q = 1.5$ Å^{-1} for several temperatures above and below T_{V_1}. The spectra are broad and featureless. On cooling there is a gradual decrease in intensity up to the transition temperature $T_{V_1} = 148.5$ K. Below this temperature there is an abrupt change in the intensity. On continued cooling down to 10 K there is a further decrease, but at 10 K scattering above the background level is still observed.

Figure 6 shows the spectra of the magnetic scattering from 0–70 meV at $Q = 3.0$ Å^{-1} above and below the valence transition. (The peak near 12.0 meV at low temperatures is due to statistical fluctuations resulting from the phonon subtraction.) We observe that the magnetic intensity extends out to at least 70.0 meV. Limited measurements were performed out to 100.0 meV, but counting times become prohibitively long. Also, there are additional inelastic peaks, perhaps due to hydrogen dissolved in the compounds,[17] which prevent any precise intensity measurements at high energies. Nonetheless, there is magnetic scattering present at energies near 100 meV.

In a cubic paramagnet the magnetic-neutron-scattering cross section may be written

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{\gamma e^2}{m_e c^2}\frac{g}{2}\right)^2 \frac{k_f}{k_i} |f(\vec{Q})|^2 2S^{zz}(\vec{Q},\omega),$$

where

$$S^{zz}(\vec{Q},\omega) = \frac{1}{2\pi}\int dt \sum_{\vec{r}} e^{i(\vec{Q}\cdot\vec{r}-\omega t)}\langle S_0^z(0) S_{\vec{r}}^z(t)\rangle,$$

$$= \frac{kT}{g^2\mu_B^2}\chi^{zz}(\vec{Q})\frac{\hbar\omega/k_B T}{(1-e^{-\hbar\omega/kT})}F^{zz}(\vec{Q},\omega),$$

$$= \frac{\hbar}{\pi}\frac{1}{g^2\mu_B^2}[n(\omega)+1]\,\mathrm{Im}\chi^{zz}(\vec{Q},\omega), \qquad (2)$$

where the symbols have their usual meaning.[18] Note that by definition $S^{zz} = S^{xx} = S^{yy}$. In the above we have assumed that the spatial part of the wave function, given in Fourier transform by the form factor $f(\vec{Q})$, is factorizable from the spin density operator $\vec{S}_{\vec{Q}}(0)$ (for a rare earth $\vec{S} \to \vec{J}$, the total angular momentum). We remind the reader in addition that if the spin dynamics are purely relaxational, $F(\vec{Q},t) \sim e^{-\Gamma(\vec{Q})t}$, then

$$F(\vec{Q},\omega) = (1/\pi)\Gamma(\vec{Q})/[\omega^2 + \Gamma^2(\vec{Q})] \qquad (3)$$

Thus apart from constants the observed neutron intensity discussed above is a measure of $S(\vec{Q},\omega)$. If we divide this by $[n(\omega)+1]$ then $\chi''(\vec{Q},\omega)$ is obtained.

Figure 9 shows the low-energy region of $\chi''(Q,\omega)$ taken at $Q = 1.5$ Å^{-1} and 3.0 Å^{-1} at $T = 250$ K in the γ phase. The data for $Q = 3.0$ Å^{-1} have been multiplied by the square of the form factor ratio:

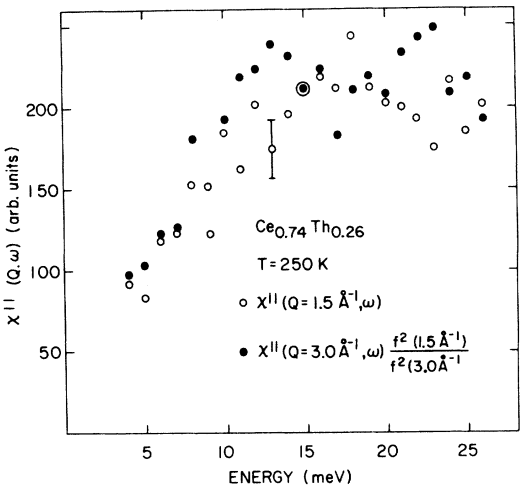

FIG. 9. The low-energy region of the imaginary part of the magnetic susceptibility for $Ce_{0.74}Th_{0.26}$ at ○ $Q=1.5$ Å^{-1} and ● $Q=3.0$ Å^{-1}. The $Q=3.0$ Å^{-1} data have been normalized by the ratio of the form factors.

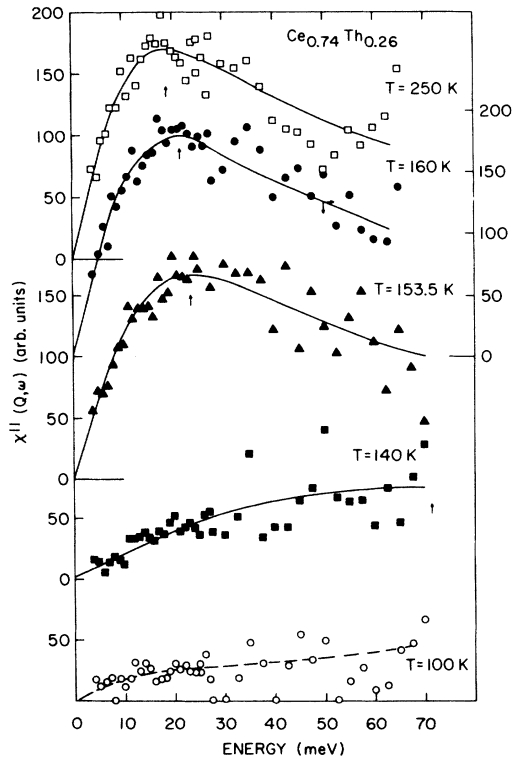

FIG. 10. Temperature dependence of the observed imaginary part of the magnetic susceptibility for $Ce_{0.74}Th_{0.26}$. The low-frequency $\hbar\omega < 27.5$ meV data were taken at $Q=1.5$ Å^{-1} and for $\hbar\omega > 27.5$ meV taken at $Q=3.0$ Å^{-1}. The data were matched in the overlapping region since in this Q region, the susceptibility is Q independent.

$|f(1.5\text{ Å}^{-1})/f(3.0\text{ Å}^{-1})|^2 = 1.32$. Within the estimated errors the dynamic susceptibilities are identical so that for these Q values $\chi''(Q,\omega)$ can be considered Q independent.

Figure 10 shows the $\chi''(Q,\omega)$ at five different temperatures. The data for $\hbar\omega < 30.0$ meV with $Q = 1.5$ Å^{-1} are taken with a PG monochromator and the data for $\hbar\omega > 25.0$ meV with $Q = 3.0$ Å^{-1} are taken with the Be monochromator. The curves have been normalized in the overlapping region $\hbar\omega \simeq 25$–30 meV. The most striking feature is the abrupt change in the shape and magnitude of $\chi''(Q,\omega)$ between the two phases. In the γ phase a peak is seen near $\hbar\omega \sim 20.0$ meV whereas in the α phase, the peak is beyond ~70 meV. The magnitude of the susceptibility shows little temperature dependence in the γ phase.

IV. DISCUSSION

In Sec. III we have described some rather complete measurements on the spin dynamics in the mixed-valence alloy $Ce_{1-x}Th_x$. In the past, neutron-scattering studies have been reported on both pure Ce and $Ce_{1-x}Th_x$. In order to clarify the relationship of our experiments to previous work and also to assist in our discussion of the overall behavior we review briefly the previous experiments. Firstly, Millhouse and Furrer,[19] in a study of γ Ce at room temperature and atmospheric pressure observe a peak at 6 meV which they identify as a Ce^{3+} crystal-field excitation. It is clear from our own results that this represents a misidentification and that the 6-meV peak must originate from the phonons. Recently, Rainford *et al.* have demonstrated explicitly from the Q dependence that the 6-meV peak arises from phonon scattering.[20] In $Ce_{1-x}Th_x$ and probably pure Ce there are no well-defined crystal-field excitations. It seems likely that the "crystal-field excitations" observed by Millhouse and Furrer[19] in *liquid* cerium also originate from vibrational excitations.

Secondly, Rainford *et al.*[20] have studied the pressure dependence of the inelastic scattering from pure Ce in the γ and α phases at room temperature. Here the phonon scattering also represents a major perturbation which must be subtracted out. After some initial ambiguity,[21] Rainford *et al.* have now[20] adopted a technique similar to ours. Their results in γ and α Ce are quite similar to ours in γ and α $Ce_{0.74}Th_{0.26}$. In γ Ce the magnetic scattering can be represented by a single Lorentzian with $\hbar\Gamma \sim 10$ meV at atmospheric pressure and ~14 meV at 6 kbars (cf. ~20 meV in $Ce_{0.74}Th_{0.26}$) while in α Ce Rainford *et al.* observe no measurable magnetic scattering for $\hbar\omega \leq 70$ meV.

Thirdly, Edelstein *et al.*[8] have reported a quasi-elastic (i.e., non-energy-discriminating) neutron

scattering study of $Ce_{0.8}Th_{0.2}$. They conclude that approximately 100 mb of magnetic scattering remain in the α phase, roughly half of that in the room-temperature γ phase. This is substantially greater than the result we find by integrating our triple-axis data (see below). We have repeated their experiment using our $Ce_{0.74}Th_{0.26}$ sample with quite similar results to theirs. However, in our case the quasielastic α phase scattering originates mainly from impurity (most likely small amounts of hydrogen) incoherent scattering. It is possible that their results have a similar explanation. In any case, in order to integrate *properly* over energy using quasielastic scattering, it is necessary to use much higher incident neutron energies than those employed by Edelstein *et al.* In addition, we have handled the problem of subtraction of the phonon scattering in a more direct manner than these authors, although their estimates correctly indicate that at moderate Q, this is an important consideration.

Finally, Holland-Moritz and co-workers[22] have carried out experiments similar to ours in $CePd_3$; this compound appears to be a mixed valence material with a fractional $4f$ valence of about 0.5 at all temperatures. Their results turn out to be closely similar to ours in γ-$Ce_{0.74}Th_{0.26}$.

We now consider various general aspects of our results. An important point to note is that both $Ce_{1-x}Th_x$, and pure Ce itself, cannot be considered as simple integral valence systems even in the γ phase. As shown in Fig. 4, at room temperature in $Ce_{0.74}Th_{0.26}$ there is a 16% departure from the 3+ state and this valence increases up to the phase transition temperature. In fact, the change in valence between room temperature and T_{V_1} is the same as the change across the first-order transition. This "mixed-valent" behavior for all temperatures must be considered in any quantitative theory for the $Ce_{1-x}Th_x$ system. We do not, of course, know how much of this originates from thermal population effects and how much reflects a true mixed-valence hybridization of the ground state.

In Fig. 7, we have shown that the magnetic scattering in the γ phase follows a form factor behavior, that is, it decreases in intensity as Q increases. In fact, the data of Fig. 7 can be represented extremely well by the calculated Ce^{3+} form factor[23] as shown by the solid line in Fig. 6. This confirms that the scattering is magnetic and further it implies that the magnetic part of the electron wave function in the γ phase, even very near the transition temperature, is the same as for a single localized Ce^{3+} ion. This is rather surprising since the valence has already changed considerably and a significant amount of $4f$-($5d$ $6s$) hybridization is expected. Measurements down to $Q = 0.3$ Å^{-1} showed no anomaly in the form factor. Clearly, one would like to obtain such data in the α phase as well. Unfortunately, this is not possible using inelastic-scattering techniques with our current sample. However, elastic-polarized-neutron studies could provide important information on the form factor in α-$Ce_{0.74}Th_{0.26}$.

We now consider the total scattering in $Ce_{0.74}Th_{0.26}$. If one has a perfect paramagnet where each spin is uncoupled and for high-enough temperature, Eq. (2) can be integrated over energy; the result obtained is

$$\frac{d\sigma}{d\Omega} = \frac{1}{3}\frac{\gamma e^2}{m_e c^2} g^2 J(J+1) f^2(Q) R(T) = 311 f^2(Q) R(T)\ \text{mb/Ce}^{3+}\ \text{atom}, \tag{4}$$

where $R(T)$ is a temperature-dependent factor which will be intimately related to $\eta(T)$, the fractional occupancy of the localized $4f^1$ configuration. From our observed spectra we can sum the intensities from -70.0 to 70.0 meV (detailed balance is used in calculating the negative energy contribution) and obtain an experimental value of $d\sigma/d\Omega$. This can be put on an absolute scale by comparing with the intensity of the incoherent scattering from vanadium, which has a known scattering cross section. For $T = 300$ K and a $Q = 1.5$ Å^{-1}[$f^2(Q) \approx 0.90$] we obtain a value of $d\sigma/d\Omega = 250 \pm 20$ mb/Ce for the paramagnetic scattering cross section at this Q. This is clearly consistent with the above theoretical value. Thus, at least at $T = 300$ K, the magnetic scattering in $Ce_{0.74}Th_{0.26}$ is consistent with that of a good paramagnet. As the temperature decreases, $d\sigma/d\Omega$ should also diminish due to the corresponding temperature-dependent decrease in the $4f^1$ fractional occupancy $\eta(T)$. Figure 11 shows the observed paramagnetic scattering in absolute units as a function of temperature. Also shown is the value calculated from Eq. (4) setting $R(T) = \eta(T)$ and $R(T) = \eta^2(T)$ with the temperature dependence of $\eta(T)$ extracted from the lattice parameter (Fig. 4). It is seen that the observed cross section decreases at a faster rate than that expected from Eq. (4) with $R(T) = \eta(T)$. One possible reason is that the scattering extends beyond the limits of our integration (70 meV) and the high-energy part may constitute a larger fraction of the total intensity as the temperature is lowered. In addition, simply setting $R(T) = \eta(T)$, as suggested by others,[8,22] is probably too naive an approximation. Indeed in the opposite limit at $T = 0$ in a coherent mixed-valent state one would expect $R(0) \sim \eta^2(0)$. In fact, the $d\sigma/d\Omega$ as T curve seems to be more consistent with $\eta^2(T)$, rather than $\eta(T)$ behavior as shown in Fig. 11. Unfortun-

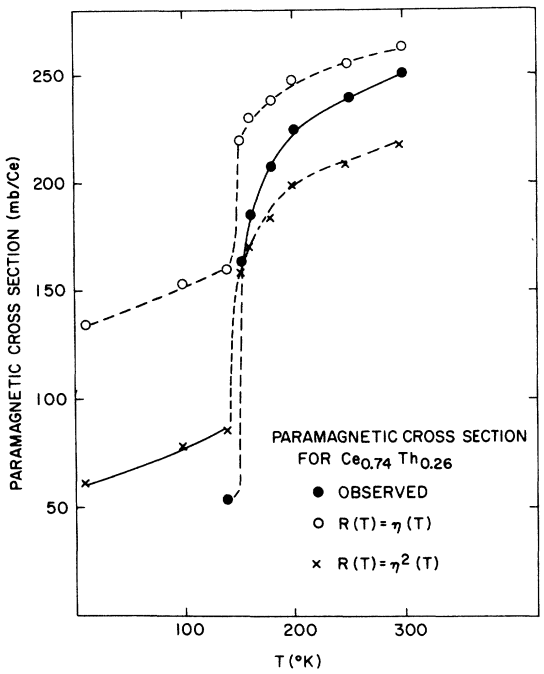

FIG. 11. Integrated magnetic scattering for $Ce_{0.74}Th_{0.26}$. The solid points are the results obtained from integrating our data. The open circles are the estimated scattering for an ideal paramagnet with the temperature dependence due to the temperature dependence of the fractional occupancy of the $4f'$ level obtained in Fig. 2.

ately, however, the data are not accurate enough nor do they extend to high enough energies to enable us to deduce unambiguously the dependence of $d\sigma/d\Omega$ on $\eta(T)$.

We shall now discuss the dynamic susceptibility deduced from our intensity measurements. The results shown in Fig. 10 were fitted with the relaxational form [cf. Eqs. (2) and (3)]

$$\chi''(\vec{Q},\omega)=C\Gamma\omega/(\Gamma^2+\omega^2), \tag{5}$$

where C is a normalization constant and Γ is a measure of the magnetization fluctuation energy. The values of C and Γ so obtained are given in Table I. The solid lines in Fig. 10 represent the best-fit curves while the small vertical arrows indicate the value of Γ obtained. For the γ phase, a good fit is obtained at all temperatures; in the α phase the peak energy has not yet been reached even at 70.0 meV so that large errors are associated with the fitted parameters. For $T=100$ K, there is too little scattering below 70 meV for one to obtain reliable parameters. At 10 K the scattering has decreased to the point where it is barely discernible above the background. We shall discuss the significance of the measured Γ below.

Firstly, however, it is of interest to compare these neutron measurements of $\chi''(\vec{Q},\omega)$ with the bulk susceptibility measurements, that is $\chi'(0,0)$, discussed in Sec. II B. From a Kramers-Kronig analysis [cf. Eq. (2)] one has

$$\chi'(\vec{Q},0)=\int_{-\infty}^{\infty}\frac{\chi''(\vec{Q},\omega)}{\omega}\,d\omega\,. \tag{6}$$

For the relaxational form Eq. (5), which empirically describes $\chi''(\vec{Q},\omega)$ quite well, one has simply

$$\chi'(\vec{Q},\omega)=C\pi\,. \tag{7}$$

In the γ phase right up to the first-order line, C is temperature independent. Thus for $Q=1.5$ Å^{-1} the static susceptibility appears to be nearly temperature independent between 300 and 153.5 K. From Fig. 2, one sees that over the same temperature range $\chi'(0,0)$ increases by about 25%. There is thus a slight Q dependence to the static response although it does not appear to be very significant. The absolute values of the susceptibility are also consistent at $Q=0$ and $Q=1.5$ Å^{-1}. Finally, as discussed in Sec. II, from the bulk susceptibility one may infer characteristic energies of the order of 12 and 130 meV in the γ and α phases, respectively. These are in reasonable agreement with the direct spectroscopic values shown in Fig. 10. We conclude therefore that the dynamic measurements at $Q=1.5$ Å^{-1} and the static measurements at $Q=0$ are closely similar to each other. This in turn implies that the spin fluctuations and, most likely, the valence fluctuations are *local* excitations in $Ce_{1-x}Th_x$.

From Figs. 4 and 10 it is evident that the most dramatic difference between the γ and the α phases of $Ce_{1-x}Th_x$ is not the fractional occupancy $\eta(T)$ but rather the spin-fluctuation energy $\Gamma(T)$. Further $\Gamma(T)$ clearly depends on $\eta(T)$ in a highly nonlinear fashion. In the α-phase, where $\Gamma\sim 0.1$ eV, the spin-fluctuation energy is comparable with the probable f^1-band energies. As noted in the Introduction, we do not yet have an adequate theoretical framework to discuss these results. It seems clear that the simplistic models applied to SmS are not

TABLE I. Parameters obtained from a least-squares fitting of our observed susceptibility to Eq. (6).

Temperature (K)	C	$\hbar\Gamma$ (meV)
300	310 ± 25	19.9 ± 1.0
250	339 ± 20	18.8 ± 1.0
200	375 ± 15	19.6 ± 0.8
160	358 ± 33	21.5 ± 1.4
153.5	331 ± 27	23.8 ± 1.4
140	140 ± 50	71.6 ± 16

rich enough in detail to describe Ce and its alloys. Most likely the γ-α transition in $Ce_{1-x}Th_x$ is best thought of as a band-to-band rather than localized-to-itinerant transition. In the γ phase, the spin-fluctuation energy $h\Gamma$ and the thermal energy kT are comparable, whereas in the α phase, our measurements show that the spin-fluctuation energy is much greater than the kT so that the spin fluctuations are barely thermally populated. However, a detailed description of the γ-α transition is complicated since all energies including the $4f$-$5d$ hybridization energy and the $5d$-band crystal-field splitting depend sensitively on the lattice constant so that the problem must be done self-consistently. There is, however, one important simplifying feature. The results here indicate that the γ-α transition is a *local* transition. Thus a real space (tight-binding) microscopic model should be adequate.

V. SUMMARY

We have presented above a detailed study on the temperature-dependent behavior of the dynamic susceptibility of the mixed-valent compound $Ce_{0.74}Th_{0.26}$ with particular care being devoted to the phonon and background subtraction. The following information is obtained from our measurements.

(i) $Ce_{0.74}Th_{0.26}$ is of mixed-valent character over a wide temperature range around the critical point.

(ii) The magnetic scattering in the γ phase, just at the transition temperature follows the atomic Ce^{3+} form factor.

(iii) The integrated intensity $d\sigma/d\Omega$ decreases as the $4f$ occupation decreases. However, no simple relation between $d\sigma/d\Omega$ and the valence can be deduced.

(iv) $\chi''(Q,\omega)$ is weakly temperature dependent in the γ phase with a peak near 20.0 meV. There is an abrupt change at T_V with the peak shifting out to beyond 70.0 meV.

(v) The $\chi'(Q,0)$ deduced from our measurements is similar to the measured $\chi'(0,0)$; this implies that the spin fluctuations are local in character.

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‡Present address: Dept. of Physics, University of California, Irvine, Calif. 92717.

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