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ABSTRACT

Highly anisotropic critical scattering associated with the transition at T_N = 49.5 K to the type-I antiferromagnetic structure has been observed in uranium nitride. The transverse susceptibility is found to be unobservably small. The longitudinal susceptibility diverges at T_N and its anisotropy shows that the spins within the (001) ferromagnetic sheets of the [001] domain are much more highly correlated than they are with the spins lying in adjacent (001) sheets. The correlation range within the sheets is much greater than that expected for a Heisenberg system with the same T_N. The rod-like scattering extended along the spin and domain direction is reminiscent of two-dimensional behaviour. The results are inconsistent with a simple localized model and may reflect the itinerant nature of the 5f electrons.

INTRODUCTION

Uranium nitride [1], a Type-I antiferromagnet below its Néel temperature (49.5 ± 0.5 K for our specimen) is a metal with an electronic specific heat coefficient [2] 35 times that of copper. The ordered moment [3] of 0.75 μ_B (along [001], the domain direction) is the lowest of the uranium pnictides correlating with the fact that UN has the smallest U-U distance of 3.45 Å. The paramagnetic susceptibility [4-8] has been interpreted as the sum of a constant Pauli part plus a Curie-Weiss part with a much larger moment of about 2.5 μ_B. This apparent paramagnetic moment need not be directly related to any real moment since the electronic ground state is unknown. A localized singlet-ground-state model ($^3H_4$) could account for the low moment, since the Γ_1-Γ_4 crystal-field splitting is expected to be of order 500 K, but cannot predict sufficient temperature dependence for the paramagnetic susceptibility. Neither can it explain the large electronic specific heat. The latter likely arises because the 5f electrons of this actinide are itinerant in nature, unlike the deep-lying 4f electrons of the lanthanide series. This is borne out by the band structure calculations of Adachi and Imoto [9]. They find, in the presence of spin-orbit and crystal-field interactions, that the extremely high density of states arises from a narrow (0.05 eV) 5f sub-band which intersects the Fermi level, contains two states per atom, and has a maximum density of states of 37 eV^{-1}. While we question the accuracy of their numerical estimates, support for an appreciable f-bandwidth and a configuration close to f^2 comes from the comparison of the small U-U distance of 3.45 Å with the Zachariasen radii [10] for uranium in the f^2(1.77 Å) and f^1(1.63 Å) state, as used by Hill [11] in his discussion of 5f localization.

The neutron measurements reported here were undertaken in the hope that the observation of sharp features in the spin-excitation spectrum would aid in the assignment of an approximate electronic ground state. The measurements showing that such sharp features are, if present, below the limits of detection, are discussed first. In the following section we describe measurements of the unusual spin correlations above T_N.

The specimen consisted of two single crystals of uranium nitride of total volume 0.8 cm^3. The neutron scattering was measured with a triple-axis spectrometer at the NRU reactor, Chalk River, operated at fixed scattered-neutron energy, E_1, and with either constant-$\vec{Q}$ or constant-ν scans.

SEARCH FOR SHARP MAGNETIC EXCITATIONS

At 4.3 K no difficulty was experienced in measuring a complete set of phonon dispersion curves [12] in the $(1\bar{1}0)$ plane. The neutron flux and crystal size were sufficient to yield intense well-resolved peaks for the LO and TO modes in the region of 12 THz. No evidence was obtained for well-defined magnetic excitations in these or separate experiments with more extended counting times. The search for magnetic excitations was carried out with different resolution (E_1 ranged from 3 THz to 10 THz) over a large wave-vector (1.3 - 7.7 $Å^{-1}$) and frequency (0 - 20 THz) range. To search for steeply rising branches, constant-ν scans were carried out through magnetic-zone centres for a series of ν values in the range 1 to 15 THz. Measurements were also made near T_N where spin-wave renormalization might lower the frequencies of any spin excitation and also well above T_N where crystal-field transitions might be expected to appear. An examination was also made of the smooth background for scattering that depended on the form factor. At all temperatures and wave vectors null results were obtained.

Possible conclusions are that the spin-wave response is (a) sharp but anomalously weak, (b) distributed over such a wide frequency range as to be essentially unobservable, or (c) mixed in with the phonon response.

CRITICAL MAGNETIC SCATTERING

In the light of these null results it was with a sense of relief that the first observations were made of critical magnetic scattering in UN. The critical scattering is the only evidence from neutron scattering to date of the occurrence of spin fluctuations in uranium nitride. The measurements were made with incident-neutron energy 7.25 THz, with 0.4° collimation before and after the specimen, and with a Ge(113) monochromator. In the $(1\bar{1}0)$ scattering plane measurements were made around (110) and (001) with no analyser and, in the (001) scattering plane, around (110), (010) and (120) with a Ge(113) analyser.

In order to help understand the results that follow we first recall that for fcc antiferromagnets the ordering occurs at inequivalent wave vectors. Thus in UN no two of the domain wave vectors, $\vec{\tau}_D$ = (100), (010) or (001) are related by a vector, $\vec{\tau}_N$, of the fcc reciprocal lattice. Consequently the critical scattering associated with the formation of each domain may separately be studied and for each the susceptibility parallel and perpendicular to $\vec{\tau}_D$, $\chi_{||}(\vec{q}\omega)$ and $\chi_{\perp}(\vec{q}\omega)$, may be obtained. The most commonly studied cubic crystals belong to the perovskite system which has a unique ordering wave vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ so that the wave-vector dependence of the separate polarization components cannot be derived from the data. Thus, more information can be obtained from critical scattering in Type-I systems.

In uranium nitride critical scattering was observed at (110) and (120). Near (001), where $\chi_{\perp}(\vec{q}\omega)$ is measured, the scattering was independent of temperature and wave vector and comparable to the scattering at (003). Thus the transverse susceptibility is unobservably small and likely non-critical. It follows that at (110) and (120), where both $\chi_{||}(\vec{q}\omega)$ and $\chi_{\perp}(\vec{q}\omega)$ may contribute, the scattering has only longitudinal character.

With the Ge(113) analyser the frequency width of the scattering well above T_N was observed to be equal to the vanadium resolution width of 0.28 THz. We estimate that the lifetime of the longitudinal spin fluctuations exceeds 14 ps. The narrow frequency width ensures that what is measured both with and without an analyser is

$$S(\vec{Q}) = f^2(Q)\int \frac{kT}{\pi\omega} \operatorname{Im} \chi_{||}(\vec{Q}\omega)d\omega = f^2(Q)\, kT \operatorname{Re} \chi_{||}(\vec{Q}\,0) .$$

The growth of $\chi_{||}(\vec{Q}\,0)$ (we drop the Re prefix in what follows) is illustrated in Fig. 1. The scattering was weak, as expected from the low ordering moment, so that measurements at this resolution above 80 K were impractical. The inverse correlation range narrows very rapidly as T_N is approached so that widths could only be extracted for $T \geq 54$ K.

At all temperatures the width in $\vec{q}$ of the scattering parallel to the [001] domain direction was much greater than the width along [110] as illustrated for 57 K in Fig. 1. To confirm that the [001] domain direction was the unique axis of the anisotropy (rather than, for example, the direction perpendicular to $\vec{\tau}$) the scattering was measured out from (110) in the (110), ($\bar{1}$10), (100) and (010) directions by orienting the specimen in the (001) scattering plane. This placed the long axis of the critical scattering out of the plane, and, as expected, the distribution of scattering in the plane was approximately circular with a width in $\vec{q}$ comparable to the (110) width in the (1$\bar{1}$0) plane. The results around (110) therefore indicate that the critical scattering has the form of an ellipsoid of revolution with major axis along the domain direction (i.e. an [001] cigar). A simple verification of this picture was provided by the results around (120), a wave vector associated with the (100) domain, where the cigar was oriented along the [100] direction.

To analyse the critical scattering T_N must first be known. Measurements were made of the (110) magnetic Bragg peak intensity for $40 \leq T \leq 50$ K. It was found to follow the power law $(T_N - T)^{2\beta}$ with $\beta = 0.31 \pm 0.03$ and $T_N = 49.5 \pm 0.5$ K.

The critical scattering above T_N was described by an anisotropic Lorentzian

$$\chi_{||}(\vec{q}\,0) = \frac{\chi_{||}(\vec{0}\,0)}{1 + q_{||}^2 / \kappa_{||}^2 + q_{\perp}^2 / \kappa_{\perp}^2}$$

which was folded with the three-dimensional resolution function [13]. At each temperature we extracted the best-fit static staggered susceptibility, $\chi_{||}(\vec{0}\,0)$, and inverse correlation lengths of the longitudinal scattering parallel, $K_{||}$, and perpendicular, $K_{\perp}$, to $\vec{\tau}_D$. The results in standard form [14] are shown in Fig. 2 and Fig. 3.

The inverse correlation length (Fig. 2) is as much as an order of magnitude smaller than the typical correlations of 3-d localized Heisenberg systems [14]. Because the cigar-shaped critical-scattering contours are reminiscent of the rods of critical scattering seen in 2-d systems [15], Fig. 2 shows also the theory for the 2-d Ising model, but the correlations in UN are of even longer range for the same reduced temperature.

The anisotropy in K is seen to be approximately independent of temperature with a mean value $K_{||} / K_{\perp} = 2.8 \pm 0.3$. Thus the spins are much more highly correlated within an (001) sheet (ferromagnetic sheet below T_N) than they are between adjacent sheets (antiferromagnetically aligned below T_N).

In Fig. 3 the resolution-corrected neutron scattering at (110), proportional to $T\,\chi_{||}(\vec{0}\,0)$, is seen to be a much more rapid function of temperature than the susceptibility of a typical pure localized-spin system.

SUMMARY AND DISCUSSION

The principal findings are as follows:

1. No spin excitations have been observed in the antiferromagnetic phase nor crystal-field excitations in the paramagnetic phase.
2. No transverse critical scattering is observed above T_N.
3. The longitudinal critical scattering corresponds to spin fluctuations that (a) are long-lived, (b) have an extremely large correlation range, (c) are more highly correlated within (001) planes than they are between planes, and (d) preserve the spin direction parallel to $\vec{\tau}_D$ for all $\vec{q}$ and T.
4. The temperature dependences of the inverse correlation range and staggered susceptibility are much more rapid than those occurring in systems of localized spins. It is not clear what significance can be attached to the large exponents obtained for a metallic system such as UN, but we note in passing that $\gamma \approx 2\nu$ is approximately satisfied. Although the results do not lie within the critical region, $(T - T_N) / T_N \sim 1/12$, the inverse correlation ranges have already fallen to the values expected for localized spin systems at temperatures that are ten times closer to T_N.

Few measurements have been made of the critical scattering of low-T_N itinerant antiferromagnets or of Type-I antiferromagnets. It is not known therefore whether either or both of these characteristics is associated with the unusual results obtained for UN. Long correlation ranges have been observed [16] in the singlet-ground-state ferromagnet $Pr_3T\ell$, where the critical scattering scales with the weakly-temperature-dependent reduced van Vleck susceptibility $[\chi_0(T_c)/\chi_0(T) - 1]$ rather than with the reduced Curie single-ion susceptibility ($\sim 1/T$). We have seen, however, that the singlet-ground-state model for UN is unpromising. It is possible, of course, that the unenhanced susceptibility of the itinerant electrons in UN is dependent only weakly on temperature, and so $K_{||}$ and $K_{\perp}$ might remain small well above T_N.

The absence of transverse critical scattering above T_N is consistent, in a negative sense, with the absence of spin-wave scattering below T_N, since both are transverse in character. Since no gap opens up in the bands of an antiferromagnet there are always single particle transitions available, in principle at least, to damp out the transverse response.

The existence of an ordered moment below a continuous phase transition does demand the existence of critical scattering of longitudinal symmetry, and this is observed. Although the crystal is cubic there is no need for the longitudinal and transverse components of staggered susceptibility to be equal as is required for the uniform susceptibility of a ferromagnet.

Anisotropic extension of the critical scattering along the domain direction and lack of renormalization of the transverse response are characteristics that have been observed previously only in two-dimensional systems [15] and in three-dimensional non-cubic antiferromagnets such as CoF_2 [17]. As UN is cubic and three-dimensional we must search for an explanation that can introduce these characteristics into the system.

Anisotropy can occur within a localized picture for a Type-I antiferromagnet because of the competition between the exchange interactions $\mathcal{J}_1$ and $\mathcal{J}_2$. Within the mean-field approximation it is, however, impossible to obtain the correct sense for the anisotropy, $K_{\parallel}^2 / K_{\perp}^2 = \mathcal{J}_2 / (\mathcal{J}_2 - \mathcal{J}_1)$, which must lie between 0 and 1 because of the constraints imposed by the stability of the Type-I structure ($\mathcal{J}_2 / \mathcal{J}_1 \leq 0$). Of course, longer-range exchange could be introduced to describe the anisotropy, but to do so immediately suggests that an itinerant description is more appropriate.

Edwards [18] has suggested that, in certain itinerant fcc 3-d magnets, the electron distribution and the spin-excitation spectrum can be partially two-dimensional in character. From the same point of view the 5f band of Adachi and Imoto [9] would appear to be highly anisotropic for wave vectors measured from the X point (the ordering wave vector of UN), being occupied along [001] (XΓ) while along [110] (XU) the band rises above the Fermi surface. One might expect that the overlap integral that gives the susceptibility falls slowly along [001] but rapidly along [110] mirroring the observed anisotropy in the susceptibility.

It is clear that the results for UN are highly unusual. It is unlikely that they can be explained by a localized spin model. Instead, the long-range correlations and their marked anisotropy and the apparent absence of spin waves indicates that it will be essential to allow explicitly for the itinerant nature of the 5f electrons in any description of the magnetic properties of uranium nitride.

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R E F E R E N C E S

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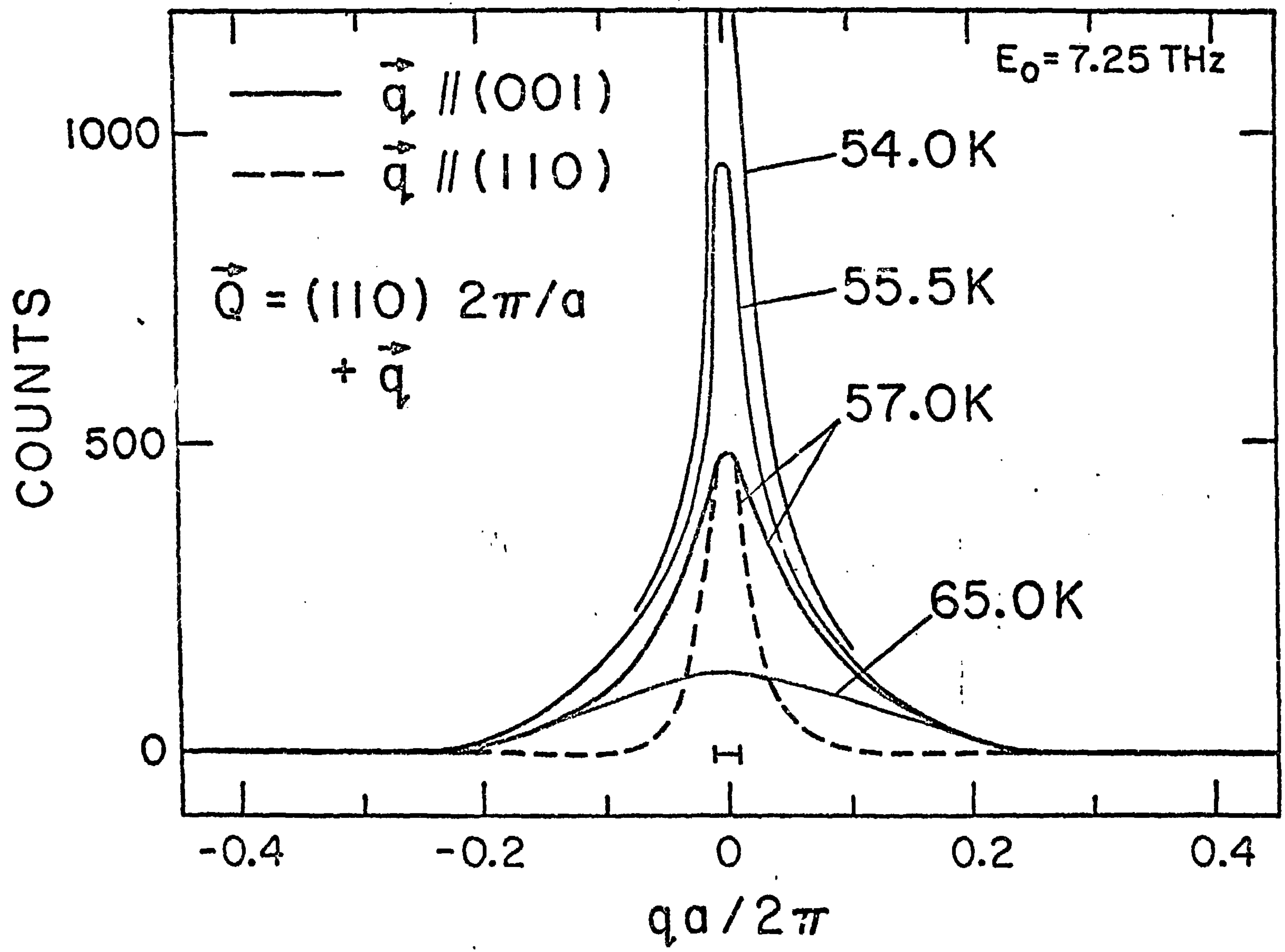
FIGURE CAPTIONS

Fig. 1. Longitudinal critical scattering in uranium nitride. The resolution width (similar for both directions) is shown by the horizontal bar.

Fig. 2. Inverse correlation length of uranium nitride times the nearest neighbour U-U distance a_{nn} = 3.54 Å.

Fig. 3. The parallel susceptibility of UN at (110) times the temperature. The line shows the susceptibility of $RbMnF_3$ [14], a typical localized-spin antiferromagnet.



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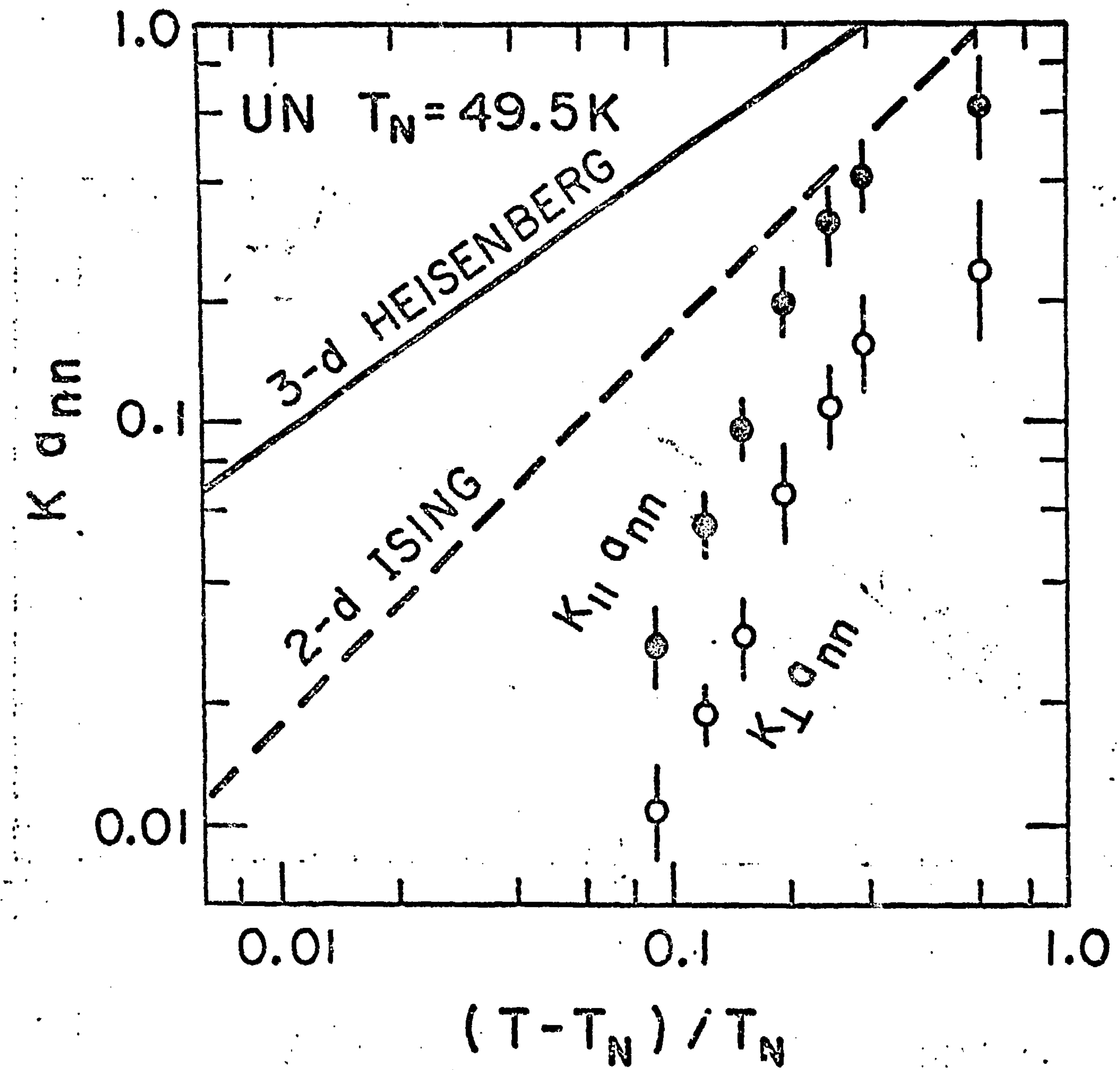

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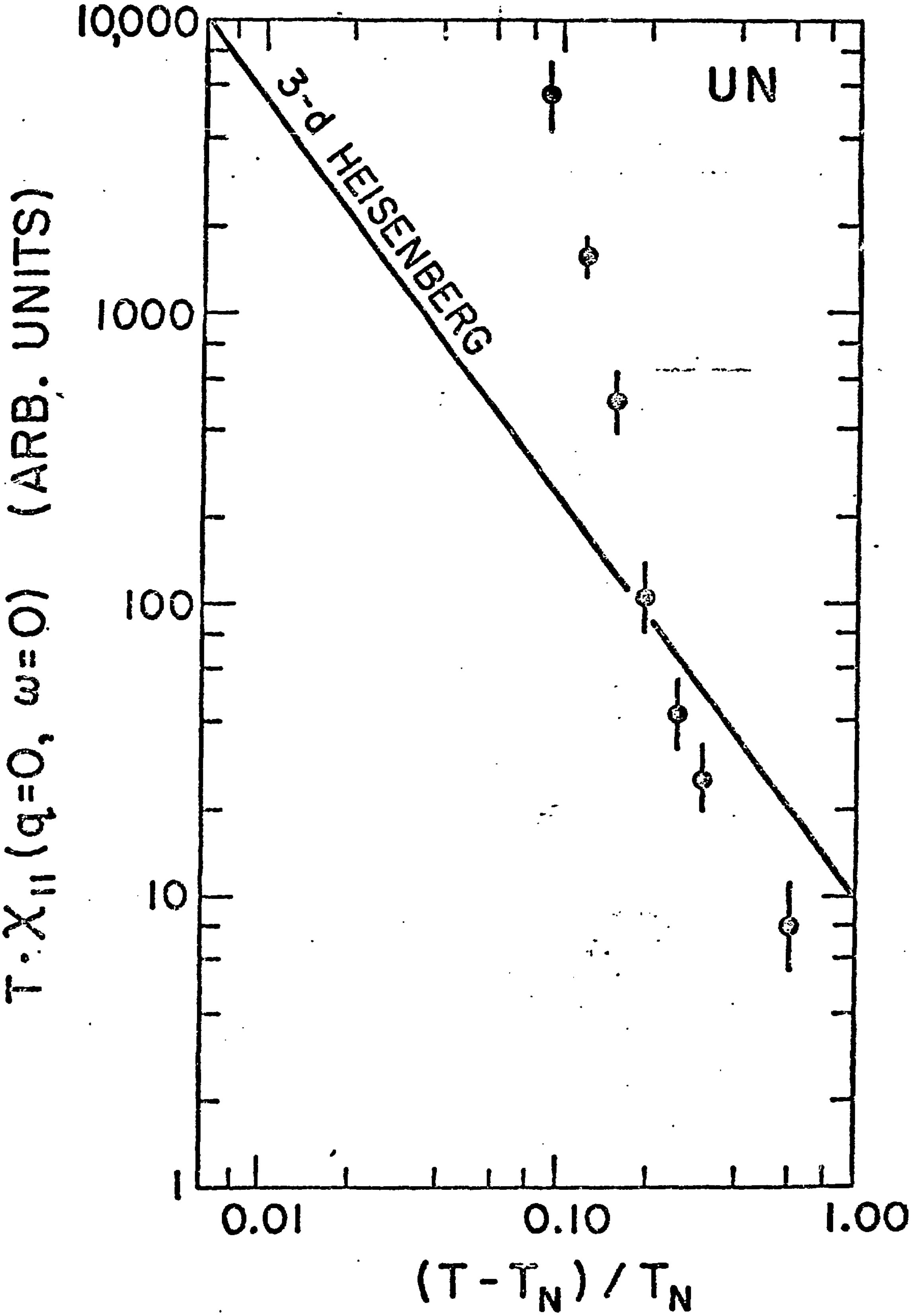

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