Observation of an unusual magnetic phase transition in $NdSn_3$

J. M. Hastings, L. M. Corliss, W. Kunnmann, R. Thomas, and R. J. Begum*
Brookhaven National Laboratory, Upton, New York 11973

P. Bak
Brookhaven National Laboratory, Upton, New York 11973
and Nordisk Institut for Teoretisk Atomfysik, Copenhagen, Denmark

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We report a neutron-diffraction study of the antiferromagnetic phase transition in $NdSn_3$. The staggered magnetization is a continuous, S-shaped function of temperature with long-range order persisting well above an "apparent" transition temperature. The transition exhibits no measurable hysteresis or critical scattering. This behavior is probably related to the fact that the corresponding $n=6$ Ginzburg-Landau-Wilson Hamiltonian possesses no stable fixed point.

Certain phase transitions, which involve a doubling of the unit cell are described by n-component vector models with $n \geq 4$.[1] It has been shown by Bak, Krinsky, and Mukamel[2] that several Ginzburg-Landau-Wilson (GLW) Hamiltonians corresponding to such systems do not possess stable fixed points in 4-ϵ dimensions. A similar analysis has been carried out independently by Brazovskii and Dzyaloshinskii for some of these models.[3] It was argued that the absence of stable fixed points indicates a first-order transition. In this way, the first-order transitions actually observed in MnO, Cr, Eu, and UO_2 were explained. We are aware of only one exception to this rule. Ott *et al.*[4] have performed neutron scattering experiments on CeSe and CeTe and they found, within experimental accuracy, a second-order transition in disagreement with ϵ-expansion calculations. Further renormalization-group calculations by Mukamel and Wallace[5] and Monte Carlo calculations by Phani *et al.*,[6] on an $n=4$ model which exhibits the structure of these materials, indicate a first-order transition. Mukamel and Wallace[5] argue that the cubic fixed point is "almost" stable and the discontinuity should be small. Even if there is evidence that the absence of a stable fixed point in 4-ϵ dimensions implies a first-order transition there is, in principle, a possibility that some *other* critical behavior might occur for real physical systems in three dimensions. The possibility of such unusual critical properties has been discussed by McCoy.[7] Indeed, for certain *random* models the runaway of the Hamiltonians in 4-ϵ dimensions has been interpreted as indicative of a "smeared" transition.[8] In particular, it has been shown[9] that this is the case for the $n > 4$ models considered in Ref. 2. Since random inhomogeneities cannot be completely avoided in real physical systems, some smearing of the first-order transition is always expected. In other words, "randomness" is a relevant parameter in the Wilson sense and should not be ignored for these systems, in contrast to $n \leq 3$ systems where the transition is expected to remain sharp.

In this paper we present a neutron-diffraction study of the staggered magnetization of $NdSn_3$. $NdSn_3$ crystallizes with the ordered $AuCu_3$ structure belonging to the paramagnetic space group $Pm3m$. The magnetic structure is sc (simple cubic) type-I antiferromagnetic, with ferromagnetic (100) planes coupled antiferromagnetically.[10] This structure corresponds to a reciprocal-lattice vector $\vec{K}_1 = (\frac{1}{2}, 0, 0)2\pi/a$, where a is the lattice constant. The magnetic unit cell is thus doubled along a [100] axis. The star of $\vec{K}_1$ consists of three vectors. The magnetization vector lies in the ferromagnetic plane, and the order parameter therefore corresponds to a two-dimensional representation of the group of $\vec{K}_1(d_{4h})$. The dimensionality of the order parameter is therefore six. This magnetic structure is very similar to the fcc type-I structure in UO_2, and we find that the GLW Hamiltonian for $NdSn_3$ is in fact identical to the one constructed by Mukamel and Krinsky[11] to describe the phase transition in UO_2. Therefore, the Hamiltonian has no stable fixed point and one should not expect a usual second-order transition. Indeed, independent Monte Carlo and high-temperature series work on a model which exhibits the same structure as $NdSn_3$ shows a first-order transition.[12]

Wintenberger and Chamard-Bois[13] have pointed out that for a cubic Bravais lattice, a collinear magnetic structure which indexes as $(\frac{1}{2}h,k,l)$, can also be indexed as a multiaxis structure on a cell which is doubled along all three axes. Extending their calculations, we have found that the most general solution, assuming all the moments to have the same magni-

tude, is given by the following possible combinations of direction cosines:

$$\alpha_1 = \alpha_2 = \pm\alpha_3 = \mp\alpha_4 \ ,$$

$$\beta_1 = \pm\beta_2 = \beta_3 = \mp\beta_4 \ ,$$

$$\gamma_1 = \pm\gamma_2 = \mp\gamma_3 = \gamma_4 \ ,$$

where atoms 1 through 4 are located at 000, $\frac{1}{2}00$, $0\frac{1}{2}0$, and $00\frac{1}{2}$, respectively, in the $2 \times 2 \times 2$ cell. Each line (taking either the upper or lower signs) represents a collinear structure. These individual structures correspond to propagation vectors $\vec{k} = (0, 0, \frac{1}{2})$ with spins either along x or y, $(0, \frac{1}{2}, 0)$ with spins along x or z, and $(\frac{1}{2}, 0, 0)$ with spins along y or z. They are precisely the six components of the order parameter and thus the renormalization-group equations together with the conclusions reached above, remain unaltered.

Samples of $NdSn_3$ were prepared in the following manner. Stoichiometric amounts of elemental Nd (99.9%) and Sn (99.9999%), sufficient for a total charge of 30 g, were reacted by the arc melting technique utilizing a nonflowing argon atmosphere at 1 atm pressure. Four remelting procedures were performed to ensure homogeneity. Using a commercial triarc (Centor), the resulting $NdSn_3$ was remelted on a water-cooled copper hearth with the three arcs symmetrically arranged. The hearth was provided with an electromagnet which, by interaction with the arcs, produced controlled stirring of the melt.[14] Several rods, a few mm in diameter and as long as 1 in. were pulled at a rate of 1 cm/h in the standard way.

The specimen used in the experiment was cut from one of the rods and consisted mostly of a single grain with typical dimensions of $\frac{1}{8}$ in. A small fraction of the sample contained other crystallites with orientations far removed from that of the main constituent and did not interfere with the measurements. The good quality of the crystal is indicated by the rocking curve for the (2,0,0) nuclear reflection shown in Fig. 1. The peak shape is quite symmetrical and narrow, with a full width at half maximum (FWHM) of 0.22°, uncorrected for instrumental broadening. As expected, trace amounts of impurity phases were detected in the sample. Nester and Schroeder[15] point out that most low-concentration rare-earth intermetallic compounds melt incongruently, producing several additional phases when cooled from the melt, but that crystals of the compound, even when they form in the presence of the other phases, tend to be pure. This tendency to form well-defined compounds is usual where the components possess widely different electronegativities. It would be expected, therefore, that crystals obtained from high-purity starting materials, as described above, would be quite pure even though trace amounts of other phases are detectable in the final product.

Neutron-diffraction data were collected with a spectrometer operated in the conventional two-crystal mode at a wavelength of 2.445 Å. Integrated intensities of the $(\frac{1}{2}, 0, 0)$ antiferromagnetic reflection were obtained from $\theta-2\theta$ scans with counting times adjusted to give approximately constant statistical accuracy as the overall intensity varied with temperature. The sample was contained in a helium cryostat mounted on an external goniometer and temperatures were controlled to ± 0.0005 K. A typical scan, taken at 4.300 K is shown in Fig. 2.

The variation of integrated intensity with temperature was found to be S shaped with a point of inflection at approximately 4.35 K and a "tail" extending beyond 5 K, as shown in Fig. 3. The region of the tail is shown in an expanded scale in Fig. 4. Peak widths remained essentially constant (FWHM $= 0.28° \pm 0.02°$) over the whole temperature range and scans showed no evidence of critical scattering. The background, taken approximately 1° in 2θ from the center of the peak, remained constant to within $\pm 2.8\%$. Even at 5 K (Fig. 5), the antiferromagnetic peak, although extremely weak, remains as sharp as those taken at lower temperatures. Measurements of

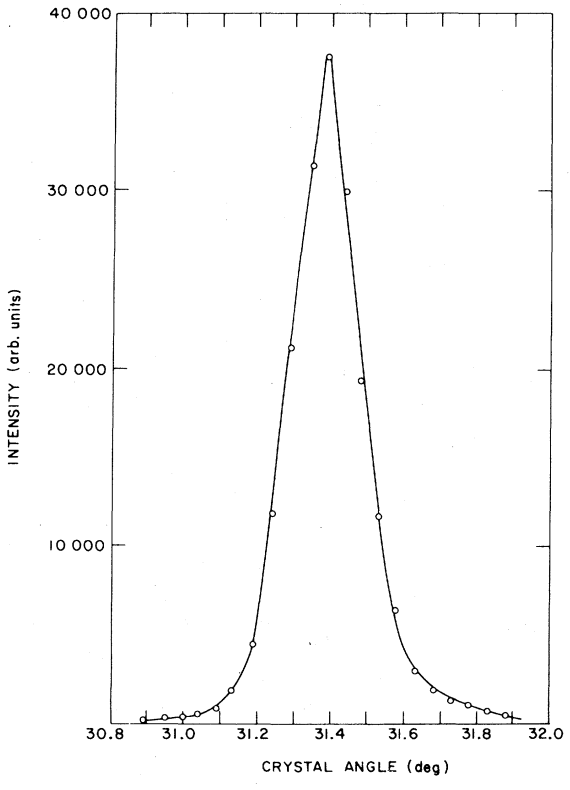

FIG. 1. Rocking curve of (2,0,0) nuclear reflection.

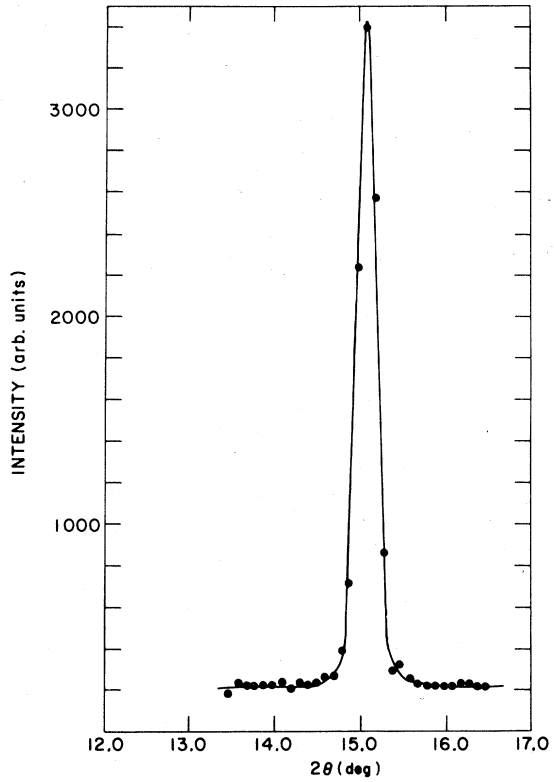

FIG. 2. Typical $\theta-2\theta$ scan of the $(\frac{1}{2}, 0, 0)$ antiferromagnetic reflection at 4.300 K.

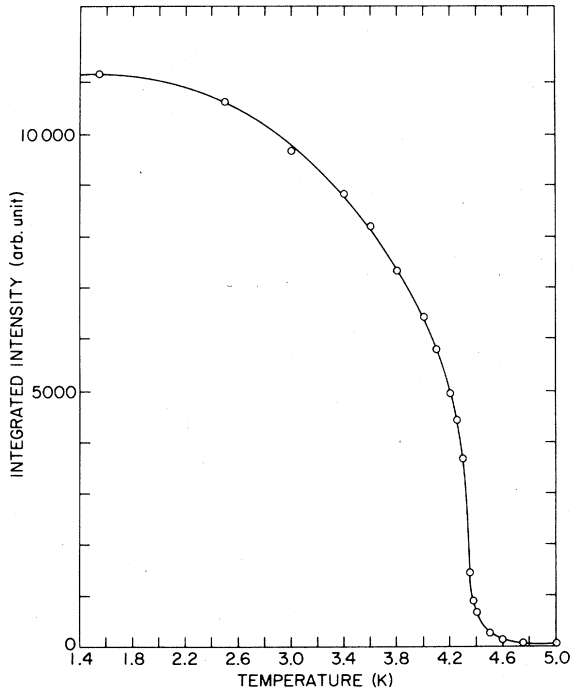

FIG. 3. Temperature dependence of the integrated intensity of the $(\frac{1}{2}, 0, 0)$ reflection.

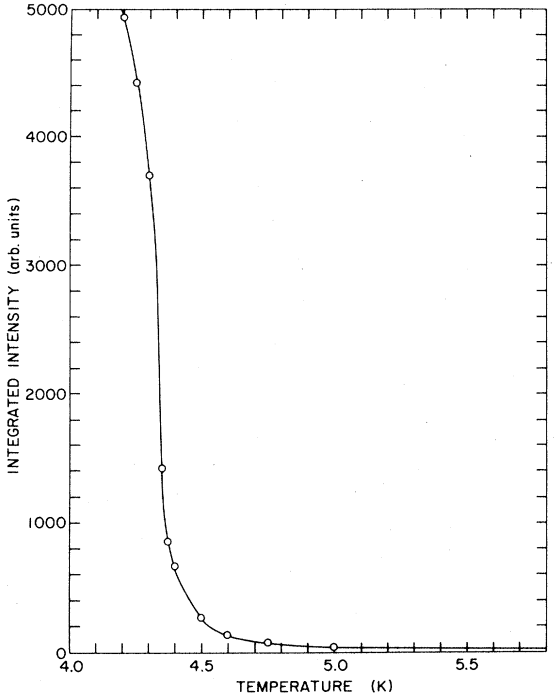

FIG. 4. Expanded-scale plot of "tail" region of Fig. 3.

peak height and background at 6 K indicated that the intensity continued to drop (reaching one-half the value at 5 K but detailed measurements at this and higher temperatures were discontinued because of the long counting times required.

The transition was tested for hysteresis by measuring the intensity at 4.320 K first after long equilibration at 6 K and then after long soaking at 1.5 K. The two measurements at 4.320 K agreed to within the statistical uncertainty of an individual measurement, which was $<1\%$. In the vicinity of 4.32 K the intensity changes by about 2% per mdeg. Thus, the apparent temperature hysteresis is <0.0005 K, which corre-

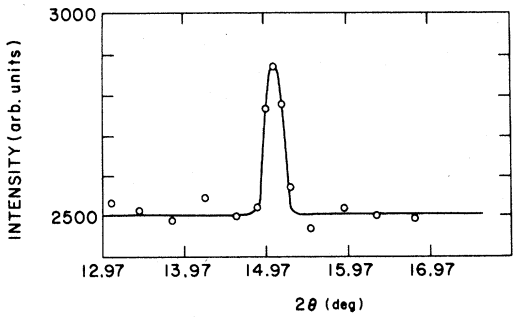

FIG. 5. $\theta-2\theta$ scan of $(\frac{1}{2}, 0, 0)$ antiferromagnetic peak at 5.00 K.

sponds closely to the precision of the temperature measurements.

Our experiment thus shows an unusual type of critical behavior which may be related to the fact that the corresponding GLW Hamiltonian does not possess stable fixed points. One possible explanation is that the peculiar S-shaped magnetization is caused by random inhomogeneities, as discussed earlier. This interpretation is consistent with the qualitative predictions of the ϵ expansion. However, the magnitude of the smearing, which is of the order of 30% of T_c, if we accept 4.35° as an approximate measure of T_c, is very hard to understand in terms of small unintended impurities in an otherwise pure system. The effects of impurities on first-order transitions have recently been discussed by Imry and Wortis.[16] They argue that an ordered cluster of size l cannot be stable at a temperature which deviates more than ΔT from the transition temperature for the pure system, where

$$\Delta T \sim [p(1-p)]^{1/2} l^{-3/2} .$$

Here p is the concentration of impurities. It is therefore very unlikely that large clusters corresponding to the very large correlation length or even long-range order, represented by the sharp peak in the tail in the experiment, can be stable over a large temperature range ΔT. Furthermore, if the effect is caused by crystal defects one would expect it to be strongly sample dependent. Another crystal, prepared by the Bridgeman technique, possessing a mosaic distribution an order of magnitude greater than that of the present sample, nevertheless showed essentially the same S-shaped behavior and magnitude of tail.

Based on the experience with several crystals, we find it very likely that the effect is indeed a genuine intrinsic property of pure $NdSn_3$. The ϵ-expansion result that the transition should be of first order would then be incomplete since it does not predict any intrinsic smearing of the transition. In this case independent calculations are needed to identify the nature of the transition. Experimental studies of similar magnetic systems would clearly also be desirable.

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*Present address: Nuclear Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

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