Crossover behavior of the magnetic phase boundary of the low-anisotropy antiferromagnet $KNiF_3$

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The ordering temperature T_c of the low-anisotropy cubic antiferromagnet $KNiF_3$ was measured as a function of magnetic field H, up to 180 kOe. At any fixed H, T_c was determined from the λ anomaly in the thermal-expansion coefficient. The transition temperature T_c increased monotonically with increasing H. At the maximum field of 180 kOe, T_c was 0.18 K higher than the Néel temperature $T_N = 246.4$ K. The observed phase boundary $T_c(H)$ is in qualitative agreement with that predicted by Fisher, Nelson, and Kosterlitz for the fully isotropic three-dimensional Heisenberg antiferromagnet. The increase of T_c with increasing H is attributed to a crossover from a Heisenberg-like transition at $H = 0$ to an XY-like transition at finite H. Magnetostriction data, taken below T_N, suggest a tetragonal lattice distortion of order 10^{-4} at $T \ll T_N$.

I. INTRODUCTION

Magnetic phase transitions in antiferromagnets have been studied experimentally and theoretically for more than two decades. Until recently the theoretical framework for understanding these phase transitions was based primarily on mean-field theory (MFT). This situation has changed in the last few years. New theoretical developments,[1] based on extended scaling and renormalization-group analysis, led to several specific predictions that differed markedly from those of the traditional MFT. Recently, some of these predictions have been confirmed experimentally.[2] One of the most striking predictions is that the ordering temperature T_c of a fully isotropic antiferromagnet should increase with increasing magnetic field H (at low H). This prediction was recently verified in the very nearly isotropic antiferromagnet $RbMnF_3$.[3-5] $KNiF_3$ is an antiferromagnet with very low anisotropy which is, however, larger than that of $RbMnF_3$. This work shows that also in this antiferromagnet, T_c increases with increasing H.

According to MFT, the ordering temperature T_c of an antiferromagnet decreases with increasing H; the predicted depression of T_c is proportional to H^2 at low H. This mean-field behavior has been observed in many antiferromagnets. However, it was recently shown by Fisher, Nelson, and Kosterlitz (FNK) that the H dependence of T_c in a *fully isotropic* three-dimensional Heisenberg antiferromagnet should be markedly different from the mean-field prediction.[1,6] The physical origin of this behavior (discussed, for example, in Ref. 5) is the change in the number of spin components which become critical at $T_c(H)$. At $H = 0$, all three spin components become critical, and the transition at $T_N \equiv T_c(H = 0)$ is Heisenberg-like. At finite H, only two spin components become critical, and the transition at $T_c(H \neq 0)$ is XY-like. The crossover from a Heisenberg-like behavior to an XY-like behavior dominates the H dependence of T_c at low H. Qualitatively, T_c is expected to increase with increasing H.[5] Quantitatively, FNK showed that (for a fully isotropic antiferromagnet at low H) T_c is given by

$$T_c - T_N = aH^{2/\phi} - bH^2 \ , \tag{1}$$

where a and b are positive constants and ϕ is the crossover exponent. The theoretical value of ϕ is 1.25.[7] Equation (1) describes a bow-shaped curve in the T-H plane, i.e., with increasing H, T_c first increases, then goes through a maximum, and finally decreases.

The predicted initial increase of T_c with increasing H is not observed in most antiferromagnets, because usually the anisotropy is sufficiently large to violate the assumption of full isotropy. For example, in the antiferromagnet MnF_2 the anisotropy singles out a unique preferred direction for the spins. In this case, only a single spin component becomes critical at the Néel temperature T_N, and the transition at $H = 0$ is Ising-like, and not Heisenberg-like. At low H, the transition in MnF_2 remains Ising-like, so that there is no crossover. In this case, T_c decreases with increasing H (at low H, and for any direction of $\vec{H}$) in qualitative agreement with MFT. Significant departures from mean-field behavior do occur near the bicritical point of MnF_2 (see Refs. 1,8, and 9), but the deviations from MFT near the Néel point are less obvious. In MnF_2 the ratio H_A/H_E between the anisotropy and exchange fields at $T = 0$ is 1.4×10^{-2}. Thus the experimental results indicate that this ratio is too large for observing the increase of T_c with increasing H, which is predicted for a fully isotropic antiferromagnet.

A different situation exists in the easy-axis uniaxial

antiferromagnet Cr_2O_3, for which $H_A/H_E \cong 3\times10^{-4}$ at $T=0$, i.e., two orders of magnitude lower than that for MnF_2. When $\vec{H}$ is parallel to the easy axis of Cr_2O_3, T_c decreases with increasing H (for low H). However, when $\vec{H}$ is perpendicular to the easy axis, T_c increases with increasing H, for fields up to 180 kOe.[10] As shown in Ref. 10, the perpendicular field configuration simulates more closely the isotropic case.

The observed H-induced increase of T_c in Cr_2O_3 stimulated the study of the H dependence of T_c in the very nearly isotropic cubic antiferromagnet $RbMnF_3$, for which H_A/H_E is a mere 5×10^{-6} at temperatures $T \ll T_N$. The study in $RbMnF_3$ fully confirmed the predictions of the FNK theory.[3-5] The present investigation of the H dependence of T_c in $KNiF_3$ was motivated by the fact that the ratio H_A/H_E for this cubic antiferromagnet ($\sim7\times10^{-5}$ at $T=0$) is intermediate between those in $RbMnF_3$ and Cr_2O_3. It was therefore expected that T_c might increase with increasing H at low H.

In this work, the H dependence of T_c in $KNiF_3$ was determined by measuring the λ anomaly in the thermal expansion coefficient at various values of H. A related series of measurements in which the H dependence of T_c in this material was determined from the λ anomaly in the ultrasonic attenuation was completed later, but a summary of the results has already been presented.[4] The two experimental procedures of determining $T_c(H)$ led to substantially the same results.

II. SOME PROPERTIES OF $KNiF_3$

$KNiF_3$ has a cubic perovskite structure, isomorphic to that of $RbMnF_3$. Each Ni^{++} ion has a spin $S=1$. The g-factor is $g \cong 2.2$.[11] The material orders antiferromagnetically at $T_N = 246$ K.[12] The magnetic order has a G-type structure, i.e, each spin is surrounded by six nearest neighbors with antiparallel spins.[13] The dominant exchange interaction is the isotropic Heisenberg exchange interaction between nearest neighbors. Using the convention in which the exchange interaction between nearest neighbors i and j is expressed as $-2J\vec{S}_i\cdot\vec{S}_j$, the exchange constant is $J/k \cong -44$ K, where k is the Boltzmann constant.[14,15] The magnitude of the exchange field at $T=0$, calculated from this value, is $H_E(0) \cong 3.6\times10^3$ kOe.

A property that is very important from the standpoint of this work is the very low anisotropy of $KNiF_3$. Below T_N, the cubic anisotropy favors an alignment of the sublattice magnetizations parallel to either one of the $\langle100\rangle$ axes. At 4.2 K the energy gap in the spin-wave spectrum is 4.5 cm^{-1}.[16] This gives an effective anisotropy field $H_A \cong 0.27$ kOe for spins nearly parallel to a $\langle100\rangle$ direction. The ratio $H_A/H_E \cong 7\times10^{-5}$ between the anisotropy and exchange fields at $T=0$ is among the lowest found in antiferromagnets. We know of only two Heisenberg antiferromagnets with lower ratios H_A/H_E, namely, $RbMnF_3$ and $TlMnF_3$.[17] The phase boundary, T_c versus H, in $RbMnF_3$ was measured recently.[3-5] Single crystals of $TlMnF_3$, of sufficient size for ultrasonic or thermal-expansion measurements, are not readily available at this time. Thus, $KNiF_3$ is one of the best materials in which one might hope to observe the predicted increase of T_c with increasing H.

At temperatures $T < T_N$, the sublattice magnetizations are parallel to one of the $\langle100\rangle$ axes. Because there are three such axes, domains with sublattice magnetizations along [100], [010], and [001] are expected to exist at $H=0$. When a magnetic field is applied along the [001] direction, the [100] and [010] domains (in which the sublattice magnetizations $\vec{M}_1$, $\vec{M}_2$ and the staggered magnetization $\vec{L}=\vec{M}_1-\vec{M}_2$ are perpendicular to $\vec{H}$) become energetically more favorable than the [001] domains. This leads to a growth of the first two types of (perpendicular) domains at the expense of the latter type of (parallel) domains. Experimentally it is found that above a certain field, H_c, only the perpendicular domains exist. The field H_c is sample dependent. Petit, Ferré, and Nouet[18] reported values of H_c between 8 and 22 kOe, and remarked that (in a given sample) H_c did not vary between 6 and 210 K. A lower value, $H_c = 5$ kOe, is quoted elsewhere.[16] These values for H_c are lower than the stability limit of $\sim$44 kOe for the "parallel" domains, deduced from the gap of 4.5 cm^{-1} in the spin-wave spectrum at 4.2 K.

We investigated the H-induced domain alignment in our $KNiF_3$ sample, using measurements of the parallel magnetostriction to detect the change in the orientations of the sublattice magnetizations. The magnetic field $\vec{H}$ was parallel to the [001] direction. The data showed that H_c varied from run to run, but did not exceed 37 kOe at 77 K, and 45 kOe at temperatures just below $T_N = 246.4$ K. Values as low as $H_c \cong 15$ kOe at 77 and 4.2 K were observed in some of the runs. On this basis it was concluded that when our sample was cooled in fields exceeding 45 kOe, the only domains which appeared at $T < T_c(H)$ were the two types of perpendicular domains.

The magnetostriction measurements in our sample also showed that the disappearance of the parallel domains (with increasing H) was accompanied by an increase in the length l of the sample along the direction of $\vec{H}$. The magnitude of this increase was $\Delta l/l \sim 9\times10^{-5}$ for temperatures $T/T_N \ll 1$. As T increased toward T_N, $\Delta l/l$ became smaller. These data suggest the existence of a tetragonal distortion (of order 10^{-4} at $T=0$) in each domain, i.e., in the ordered phase the lattice constant along the direction of the staggered magnetization $\vec{L}=\vec{M}_1-\vec{M}_2$ is shorter than the lattice constant for directions perpendicular to $\vec{L}$.

III. EXPERIMENTAL TECHNIQUES

All measurements were performed on a $KNiF_3$ single crystal, kindly provided by H. J. Guggenheim. The ordering temperature T_c was determined as a function of H by measuring the λ anomaly in the thermal-expansion coefficient at various fixed values of H, up to 180 kOe. The magnetic field was produced by a Bitter-type solenoid, and was always parallel to the [001] crystallographic direction. The length $l(H,T)$ which was measured in these experiments was the linear dimension of the sample along the [001] direction. This length was 3.63 mm at room temperature. The Néel temperature of our sample was $T_N = 246.4 \pm 0.2$ K, where the uncertainty represents the absolute accuracy (rather than the precision).

The thermal expansion measurements were carried out with a capacitance dilatometer made of copper, as in Ref. 3. The capacitance cell was surrounded by a copper can filled with helium exchange gas. This inner can was surrounded by a second copper can, from which it was separated by a vacuum space. The outer can was immersed in a bath of Freon-12 (CCl_2F_2) whose normal boiling point is 243.4 K, i.e., 3 K below T_N. A small heat leak between the capacitance cell and the Freon bath caused the temperature of the capacitance cell to drift slowly toward that of the bath. The drift rate could be varied by changing the temperature of the bath. The bath temperature was controlled by adjusting the vapor pressure with a mechanical pump and a pressure regulator. Final data were taken in the following manner. The capacitance cell was first heated to a temperature slightly above $T_c(H)$, using a heater wound on the outer surface of the inner can. Subsequently, the heater was turned off, and the temperature dependence of l was recorded on a punch tape as the sample cooled slowly toward the temperature of the Freon bath. Some checks were made, however, by taking data as the temperature increased slowly. This was accomplished either by using the heater, or by increasing the vapor pressure of the Freon bath sufficiently above atmospheric pressure so that the boiling point was above $T_c(H)$.

Temperatures were measured with a thermistor resistance thermometer, which had a resistance of $\sim 4 \times 10^3$ Ω near T_N, and a sensitivity of -4.7 %/K. This thermometer was embedded in a copper block that was a part of the capacitance cell. The thermistor thermometer was calibrated *in situ*, at $H = 0$, against a platinum resistance thermometer which was mounted on the same copper block. The magnetoresistance of the thermistor was measured near T_N by stabilizing the temperature and measuring the changes in the resistance as H was changed from zero to a given value and then back to zero. In these measurements, the temperature was stabilized in either of two ways: (i) by maintaning a constant heat input (with the Freon bath at atmospheric pressure), or (ii) by increasing the vapor pressure of the bath until the boiling point was very near T_N. Both procedures gave the same results, within the experimental accuracy. The magnetoresistance measurements were also repeated with the sample removed from the capacitance cell (to avoid possible magnetocaloric effects), which produced no observable change in the results. The magnetoresistance was negative and was proportional to H^2. At 180 kOe this magnetoresistance was equivalent to $+(92 \pm 2)$ mK. All the data were corrected for this magnetoresistance. The precision of the measurements of $T_c(H)$ was estimated as 10–20 mK, depending on the particular experimental run.

All data for $l(H,T)$ versus T, at a fixed H, were differentiated numerically with respect to T, in order to obtain the thermal-expansion coefficient $(1/l)(\partial l/\partial T)$. Two procedures were then used to obtain the H dependence of T_c. In the first, the temperature at the maximum of $\partial l/\partial T$ was identified as $T_c(H)$. In the second, the "rounding" of the λ anomaly was estimated, and $T_c(H)$ was identified as the temperature where the maximum in $\partial l/\partial T$ would have been in the absence of such rounding. (The rounding was partly intrinsic to the sample, and partly a result of the differentiation procedure.) The results for the H dependence of T_c obtained with both procedures were in very good agreement with each other. The results for $T_c(H)$ that are presented in Sec. IV are the average of the results obtained with these two procedures.

IV. RESULTS AND DISCUSSION

The thermal-expansion coefficient $(1/l)(\partial l/\partial T)$ was measured at fixed values of H, up to 180 kOe. The magnetic field was always parallel to the [001] axis. A λ anomaly in $\partial l/\partial T$ versus T was observed at all fields. An example of this anomaly is shown in Fig. 1. The phase boundary T_c vs H, determined from the thermal expansion data as described in Sec. III, is shown in Fig. 2. In this figure, H is the internal magnetic field (the correction due to the demagnetizing field was a mere 0.03%). It is apparent that T_c increases with increasing H, in qualitative agreement with the prediction of FNK, but in disagreement with MFT.

The values of $T_c(H)$ for $H > 45$ kOe correspond to transitions from the disordered (paramagnetic) phase to the ordered (antiferromagnetic) phase for the perpendicular domains, i.e., the [100] and [010] domains in which the staggered magnetization $\vec{L}$ is perpendicular to $\vec{H}$. The situation for fields below 45 kOe is more complicated because in the ordered phase there may exist parallel domains, with $\vec{L} \parallel \vec{H} \parallel [001]$, in addition to the perpendicular domains. The transition temperature for the parallel domains is expected to differ from that for the perpendicular domains, except

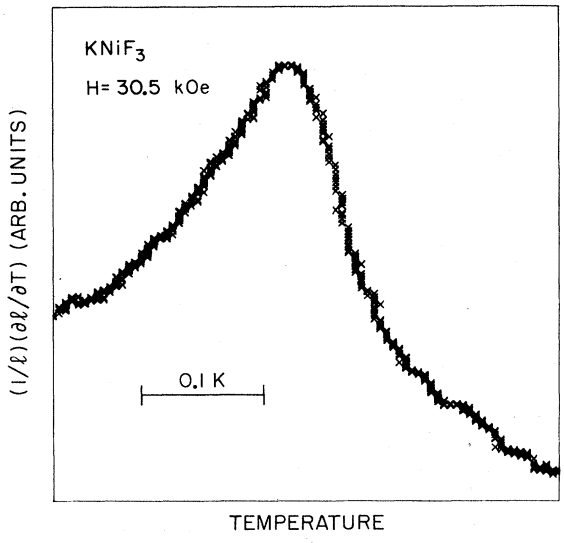

FIG. 1. λ anomaly in the thermal-expansion coefficient $(1/l)(\partial l/\partial T)$ at $H=30.5$ kOe. The magnetic field $\vec{H}$ is parallel to [001].

at $H=0$. Therefore, one might expect that at fields below 45 kOe there are two transition temperatures. However, no evidence for two such separate transitions was observed in the present work. This may be explained as follows. For fields well below 45 kOe, the estimated difference between the two transition temperatures does not exceed several mK, and the

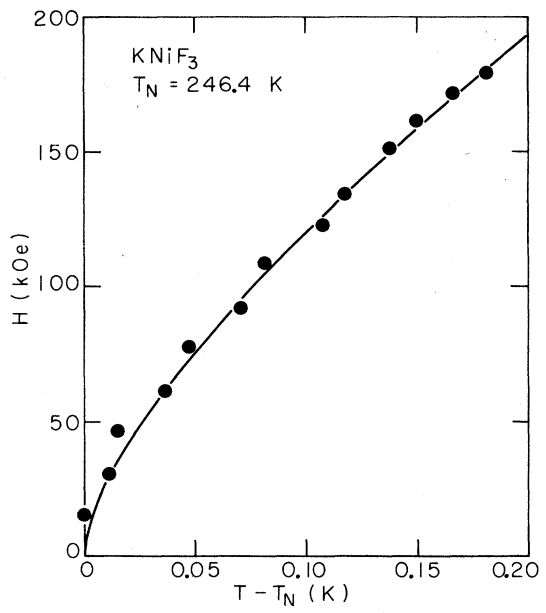

FIG. 2. Variation of the ordering temperature T_c of $KNiF_3$ with H. The magnetic field $\vec{H}$ is parallel to [001]. The solid curve is a fit of the data above 50 kOe to Eq. (1). In this fit, ϕ is held fixed at its theoretical value 1.25 while a and b are treated as adjustable parameters.

two transitions are not resolved experimentally. For fields close to 45 kOe, the estimated difference between the two transition temperatures is comparable to the experimental resolution. However, at these fields the volume occupied by the perpendicular domains was much larger than that occupied by the parallel domains, so that the λ anomaly for the perpendicular domains dominated the experimental results.

For the ideal fully isotropic antiferromagnet, the staggered magnetization in the ordered phase and at a finite magnetic field is always perpendicular to $\vec{H}$. Therefore, the phase boundary $T_c(H)$ for the perpendicular domains in $KNiF_3$ is expected to resemble that of the fully isotropic antiferromagnet. The observed increase of T_c with increasing H, shown in Fig. 2, confirms this expectation, and lends further experimental support to the FNK theory.

In the case of $RbMnF_3$ it proved possible to obtain a precise value for the crossover exponent ϕ by fitting the phase boundary $T_c(H)$ to Eq. (1).[3–5] The situation in $KNiF_3$ is less favorable in this regard, for two reasons: (i) The exchange field (at $T=0$) in $KNiF_3$ is larger than that in $RbMnF_3$ by a factor of ~4.5. At $T=0$ the transition from the ordered phase to the disordered (paramagnetic) phase should occur at $2H_E(0)$, or roughly 7×10^3 kOe in $KNiF_3$. The data for $T_c(H)$ in Fig. 2 represent, therefore, a very small segment of the total phase boundary. A fit of such a small segment to Eq. (1), and taking into account the experimental uncertainties, leads to rather imprecise values for the adjustable parameters a, b, and ϕ. (ii) In an antiferromagnet for which the anisotropy is very small but nonzero, Eq. (1) may not be valid except for fields that are large compared to the instability field for the parallel domains (which corresponds to the spin-flop field for a uniaxial antiferromagnet). For $KNiF_3$, this instability field is ~44 kOe at $T=0$. Thus the maximum field used in the present experiments was larger than the instability field by only a factor of ~4. This makes the applicability of Eq. (1) doubtful.

In spite of the above limitations, we have carried out fits of the data in Fig. 2 to Eq. (1). Only data above 50 kOe, which clearly correspond to the perpendicular domains were included. A fit in which a, b, and ϕ were allowed to vary gave $\phi=1.27$. However, the standard deviation for ϕ was $\sigma_\phi=0.46$, which indicated that the data were insufficiently precise and/or insufficiently extensive for obtaining a meaningful value for ϕ. Another fit, in which ϕ was held fixed at its theoretical value 1.25 but in which a and b were allowed to vary, was also carried out for the data above 50 kOe. The results of this fit are shown as a solid curve in Fig. 2. The rms deviation of the data points above 50 kOe from this solid curve is 3.15 mK.

In conclusion, the measured phase boundary in $KNiF_3$ confirms the recently predicted initial increase

of T_c with increasing H for isotropic antiferromagnets. However, an accurate value for the crossover exponent ϕ cannot be obtained from these data.

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