NASA TECHNICAL MEMORANDUM

NASA TM X-52997

NASA TM X-52997

PHASE TRANSITIONS AND MAGNETOSTRICTION IN $CsMnCl_3 \cdot 2H_2O$

by John A. Woollam and Paul R. Aron
Lewis Research Center
Cleveland, Ohio

TECHNICAL PAPER proposed for presentation at
American Physical Society Meeting
Cleveland, Ohio, March 29 - April 2, 1971

E-6240

PHASE TRANSITIONS AND MAGNETOSTRICTION IN $CsMnCl_3 \cdot 2H_2O$

John A. Woollam and Paul R. Aron

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

ABSTRACT

Dimensional changes (strain) along the three principle crystal axes are studied as a function of magnetic field and temperature in the antiferromagnetic, spin flopped, and paramagnetic phases. Changes in dimensions are examined through the phase transitions between the magnetic states.

I. INTRODUCTION

Magnetostriction is the fractional change $\Delta l/l$ in length l of a material caused by the presence of a magnetic field. This change is called strain, and is commonly designated by ϵ $(= \Delta l/l)$. Magnetostriction effects are large and have been extensively studied in ferromagnets [1]. There have also been some studies of the effects in diamagnetic materials, for example, bismuth [2]. Results on antiferromagnetic CoO were reported by Nakamichi [3] and on NiO by Belov and Levitin [4]. We have, however, been unable to find any previously reported magnetostriction measurements on spin-flopped antiferromagnets.

$CsMnCl_3 \cdot 2H_2O$ crystals grow with plane parallel faces and cleave with faces which are parallel to the principle planes, an ideal configuration for the parallel plate capacitance method [5].

$CsMnCl_3 \cdot 2H_2O$ also exhibits spin-flopped antiferromagnetism at conveniently low magnetic fields. The magnetic phase boundaries have been determined up to 10 tesla (1T = 10 kG) by Butterworth and Woollam [6] and the phase diagram is shown in Fig. [1].

Magnetic susceptibility [7] and specific heat [8] measurements have shown that there are two zero field ordering temperatures. The first is near 20 K where NMR measurements [9] show that spins align antiferromagnetically in linear chains coupled in two dimensions. At 4.88 K there is a phase transition to a three dimensional antiferromagnetic state.

With a magnetic field less than about 1.7 tesla oriented along the $\hat{b}$ direction (axes were defined by Jensen, et al. [10]) the spins are antiparallel along the field direction. Above 1.7 tesla the spins flop from the $\hat{b}$ direction to a direction in the perpendicular ($\hat{a}\hat{c}$) plane. The spins still are ordered antiferromagnetically, that is, are still antiparallel to each other. Spin flopping was first predicted by Néel [11] and later observed by Gorter [12] in $CuCl_2 \cdot 2H_2O$. For a general discussion of spin flopping see Morrish [13].

II. EXPERIMENTAL METHODS

We use the parallel plate capacitance method developed by White [5]. One plate of the capacitor is glued to the top of the sample and its capacitance with respect to a fixed plate is measured with an ac capacitance bridge. A lock-in-amplifier is used as a null detector and the off-balance voltage is a measure of the strain. The same apparatus was used to detect de Haas-van Alphen type oscillations of the strain in bismuth and PbTe [14], and can detect strain of 10^{-10} with a one to one signal to noise ratio.

Two magnets were used. A split pair superconducting magnet [15] was used for transverse (strain (ϵ) not parallel to the magnetic field) measurements. For longitudinal (ϵ parallel to the magnetic field) measurements, a 10 tesla (1T = 10 kG) superconducting solenoid was used. Temperatures down to 1.08 K were achieved by pumping on the liquid helium bath. Temperatures above 4.2 K were obtained by heating the capacitance cell. Temperatures were measured with a carbon thermometer calibrated against the vapor pressure of He^4.

Crystals of $CsMnCl_3 \cdot 2H_2O$ were grown from a solution of equal parts of CsCl and $MnCl_2 \cdot 2H_2O$. Crystals were then refrigerated

to prevent gain or loss of water over long periods of time. Crystal axes were crudely found by visual observation of cleavage planes. An accurate determination, within ±0.1 degree, was obtained from the symmetry of experimental results as a function of angle.

For all experiments the field was located along or close to the $\hat{b}$ axis. Strains were then measured in the mutually perpendicular $\hat{a}$, $\hat{b}$, and $\hat{c}$ directions.

III. EXPERIMENTAL RESULTS

A. $\hat{c}$ Axis Magnetostriction

In Fig. [2] the strain along the $\hat{c}$ direction is plotted as a function of magnetic field. In the top half of the figure the data was taken at 1.08 K. The $\hat{c}$ direction strain increases with magnetic field for fields below 1.8 tesla. In this region of field and temperature the sample is antiferromagnetically ordered as shown in Fig. [1]. For fields well below the phase transition ($H < 0.8\ H_c$ where H is magnetic field, H_c is the phase transition field) the field dependence of strain, ϵ, is

$$\epsilon \propto H^n \qquad (1)$$

where $n = 2.0 \pm 0.2$.

At 4.2 K the $\hat{c}$ axis strain has $n = 2.5 \pm 0.2$ but <u>decreases</u> with increasing field below H_c. At the phase transition, H_c, there is a sharp increase in the $\hat{c}$ dimension for all temperatures. Note, however, that the 4.2 K scale is an order of magnitude smaller than the 1.08 K scale.

The sharpness of the strain spike permits accurate identification of the fields for the transition, and data for several temperatures is plotted in Fig. [1]. Scatter in these points is due to drift in the integrator used to measure magnetic fields, and systematic differences are possibly due to differences in sample orientation.

Above H_c (fig. 2) the strain dependence on field did not follow a simple power law. At 1.08 K the strain appeared to saturate to a constant value as a function field.

B. $\hat{b}$ axis magnetostriction

The $\hat{b}$ axis strain is measured parallel to the direction of the magnet field. In Fig. [3] the strain is plotted as a function of field to 9 tesla at 4.2 K. In this direction the n from Eq. (1), for $H < H_c$ is $2.2 \pm 0.1 + 4.2$ K. There is little qualitative change in the character of the curve as a function of temperature. At lower temperatures the phase transition peak shifts to lower fields and sharpens. This is shown inset in Fig. [3]. The $\hat{b}$ dimension increases in the antiferromagnetic state and decreases in the spin flopped state. At 4.2 K the $\hat{b}$ strains are larger than the $\hat{c}$ strains shown in Fig. [2]. At low temperatures the $\hat{b}$ strains are several times smaller than the $\hat{c}$ strains.

C. $\hat{a}$ Axis Magnetostriction

In Fig. [4] the $\hat{a}$ strain is plotted as a function of magnetic field to 3 tesla for temperatures of 1.24 K and 4.2 K. The strain in this direction can also be written

$$\epsilon \propto H^n \qquad (2)$$

where at 4.2 K $n = 2.2 \pm 0.1$ and at 1.24 K $n = 2.6 \pm 0.2$.

Also shown in Fig. [4] is the dependence on the angle between H and the $\hat{b}$ axis at 4.2 K, of the sharpness of the phase transition spike. The alignment is extremely critical in this orientation since with H only a few degrees from $\hat{b}$ the phase transition is very difficult to observe. At 1.24 K the phase transition is slightly easier to observe. This contrasts with the $\hat{c}$ axis magnetostriction where the phase transition was very easy to detect and became more pronounced at low temperatures.

From the observed change in three mutually perpendicular dimensions we have calculated the volume change with magnetic field. For $H < H_c$ the volume increases as

$$\frac{\Delta v}{v} \propto H^m \qquad (3)$$

where $m = 2.1 \pm 0.2$, and has a sharp positive spike at the phase

transition from antiferro magnetic to spin flopped antiferromagnetic states.

D. Further Results

As shown in Fig. [1] a change in field at fixed temperatures between 4.36 K (triple point) and 4.88 K (Néel temperature) takes the sample through three phases. At low fields the sample is antiferromagnetic. At intermediate fields it is paramagnetic, and at high fields it is spin flopped-antiferromagnetic. Examples of the strain changes in these three magnetic states are shown in Fig. [5] for temperatures of 4.67 K and 4.76 K. The knees in the plots of strain as a function of field delineate the phase boundaries for antiferro-to paramagnetic and spin-flopped to paramagnetic states.

A more accurate method of determining the phase boundaries bordering the paramagnetic phase is to fix the magnetic field and heat the sample. The dimension changes are then a measure of thermal expansion. The thermal expansion shows a knee at the phase boundary as illustrated in Fig. [6] for $\hat{c}$ axis strains. Although the copper sample holder has a very weak dependence of strain on magnetic field, it has a significant thermal expansion. Thus Fig. [6] is a plot of the observed thermal expansion difference between the cell and the sample. The knee at the phase transition is easily observed however.

In the antiferromagnetic-to-spin flopped phase transition a hysteresis was observed. That is, the field H_c was not the same for increasing as for decreasing fields. The difference was on the order of 1 percent, and independent of angle between H and $\hat{b}$ for H in the $\hat{b}$ - $\hat{a}$ plane ($\hat{c}$ axis magnetostriction).

IV. DISCUSSION

Magnetostriction in ferromagnets has been observed and theoretically predicted to be quadratic in magnetic field [2]. In the work on bismuth [3] it was demonstrated that the magnetostriction was nearly

proportional to H^2 for a diamagnet, and similarly for antiferromagnetic CoO. It is not surprising then, that for $CsMnCl_3 \cdot 2H_2O$ the strain exhibits a dependence on field only slightly greater than quadratic.

The phase diagram determined by the present measurements is consistant with that found by Butterworth and Woollam. On the antiferromagnetic to spin flopped boundary the $\hat{b}$ axis data agrees well with Ref. 5. The errors in the $\hat{c}$ axis data arise mainly from integrator drift during field measurements. On the spin-flopped to paramagnetic boundary, difficulty in calibrating thermometers was the major source of errors. Systematic differences with the results of Ref. 5 could also be due to differences of sample alignment.

The antiferromagnetic to spin-flopped antiferromagnetic phase transition has very pronounced effects on strains, as seen in Fig. [2], for example. This is consistent with this transition being of 1st order [17]. First order transitions have associated latent heats [17], and hysteresis effects could result.

We found that the spin-flop transition for increasing magnetic field was one percent higher in field than the transition for decreasing field. Forstat (private communication) suggests that this is not a true hysteresis but rather that it is due to crystal misalignment in the magnetic field. We have investigated the transition in increasing and decreasing fields, for a series of angles between the field and crystal axes. Over a ranged ±30 degrees from H along $\hat{b}$ the hysteresis is about the same. If misalignment were the cause, then the hysteresis should depend strongly on angle. The hysteresis effect was seen using both the transverse and the longitudinal magnets, and was still present on sweeping the field very slowly through the phase transition. Thus, the effect appears to be real.

The behavior of the strain through the phase transition from antiferromagnetic or spin-flopped antiferromagnetic to paramagnetic regions (fig. 6) appears to be of second order, since only a knee [17] in the strain vs. temperature curve is found.

REFERENCES

1. E. Callen, H. Callen, Phys. Rev. 139, A 455 (1965).
2. D. Shoenberg, Proc. Roy Soc. A 135, 537 (1932).
3. T. Nakamichi, J. Phys. Soc. Japan 20, 720 (66).
4. K. P. Belov and R. Z. Levitin, JETP 37, 565 (1959).
5. G. K. White, Cryogenics 1, 151 (1961).
6. G. J. Butterworth, J. A. Woollam, Phys. Letts. 29A, 259 (1969).
7. T. Smith and S. A. Friedberg, Phys. Rev. 176, 660 (1968).
8. H. Forstat, J. N. McElearney, and N. D. Love, private communication.
9. R. D. Spence, W. De Jonge, and K. V. S. Rama Rao, J. Chem. Phys. 51, 4694 (1969).
10. S. T. Jensen, P. Anderson, R. S. Rasmussen, Acta Chem. Scand. 16, 1890 (1962).
11. L. Néel, Ann. De Physique 5, 232 (1936).
12. C. J. Gorter and T. Van Peski-Tinbergen, Physica 22, 273 (1956).
13. A. H. Morrish, The Physical Principles of Magnetism, John Wiley and Sons, Inc., New York, 1965.
14. P. R. Aron and B. S. Chandrasekhar, Phys. Letts. 30A, 86 (1969).
15. J. C. Laurence, NASA TN D-4910, (1968).
16. M. E. Fisher, in Reports on Progress in Physics, Institute of Physics and the Physical Society London 1967, p. 615.
17. M. W. Zemansky, Heat and Thermodynamics, McGraw-Hill Book Co., Inc. New York, Toronto, London, 1957, p. 317.

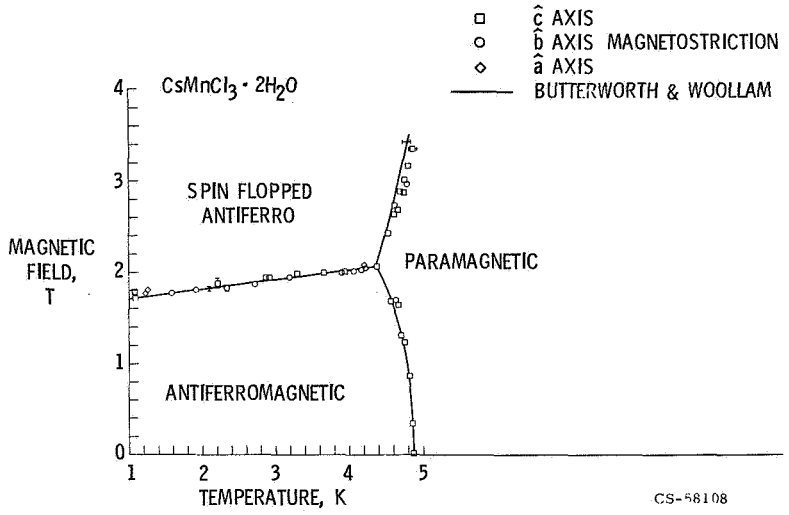

FIGURE 1. - MAGNETIC PHASES, $CsMnCl_3 \cdot 2H_2O$.

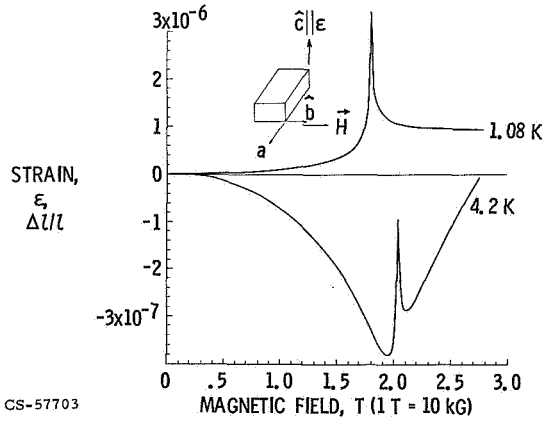

FIGURE 2. - $\hat{c}$ AXIS MAGNETOSTRICTION.

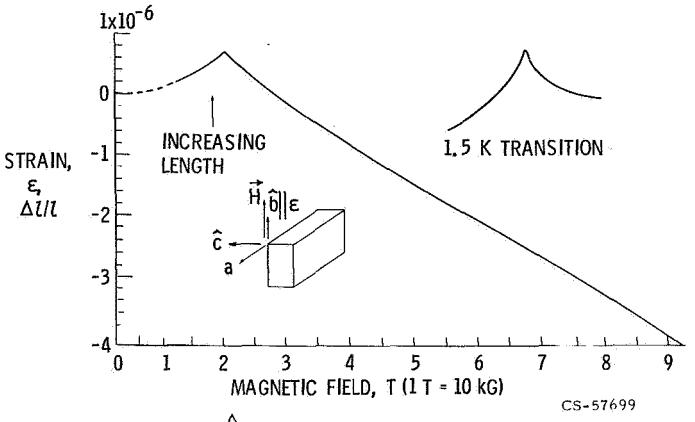

FIGURE 3. - $\hat{b}$ AXIS (LONGITUDINAL) MAGNETOSTRICTION 4.2 K.

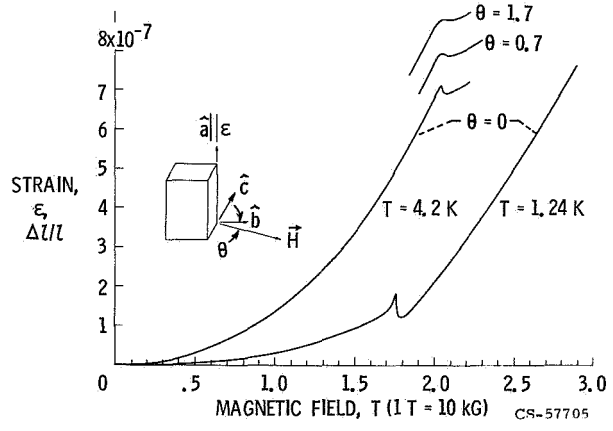

FIGURE 4. - C-AXIS MAGNETOSTRICTION IN $CsMnCl_3$-$2H_2O$.

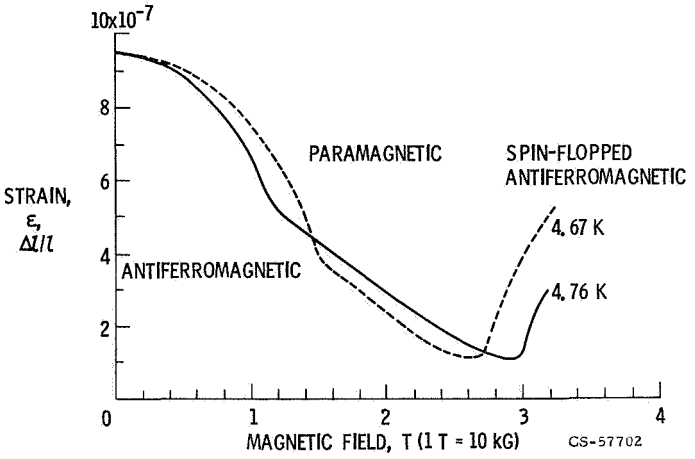

FIGURE 5. - $\hat{c}$-AXIS MAGNETOSTRICTION.

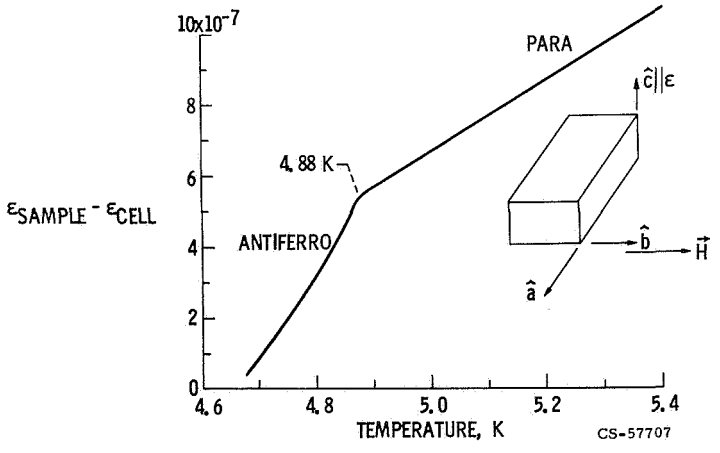

FIGURE 6. - $\hat{c}$ AXIS, ZERO FIELD THERMAL EXPANSION.

NASA-Lewis