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# Magnetic ordering of the antiferromagnet $\text{Cu}_2\text{MnSnS}_4$ from magnetization and neutron-scattering measurements

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Magnetization and neutron-diffraction measurements were performed on a single crystal of  $\text{Cu}_2\text{MnSnS}_4$ . This quaternary magnetic semiconductor has the stannite structure (derived from the zinc-blende structure which is common to many II-VI dilute magnetic semiconductors), and it orders antiferromagnetically at low temperature. The neutron data for the nuclear structure confirm that the space group is  $I\bar{4}2m$ . Both the neutron and magnetization data give  $T_N=8.8$  K for the Néel temperature. The neutron data show a collinear antiferromagnetic (AF) structure with a propagation vector  $\mathbf{k}=[1/2,0,1/2]$ , in agreement with earlier neutron data on a powder. However, the deduced angle  $\theta$  between the spin axis and the crystallographic  $c$  direction is between  $6^\circ$  and  $16^\circ$ , in contrast to the earlier value of  $40^\circ$ . The magnetization curve at  $T \ll T_N$  shows the presence of a spin rotation (analogous to a spin flop), which indicates that the spin axis is indeed close to the  $c$  direction. The deduced magnetic anisotropy gives an anisotropy field  $H_A \cong 2$  kOe. At high magnetic fields the magnetization curve at  $T \ll T_N$  shows the transition between the canted (spin-flop) phase and the paramagnetic phase. The transition field,  $H=245.5$  kOe, yields an intersublattice exchange field  $H_E=124$  kOe. The exchange constants deduced from  $H_E$  and the Curie-Weiss temperature  $\Theta=-25$  K show that the antiferromagnetic interactions are an order of magnitude smaller than in II-VI dilute magnetic semiconductors (DMS's). The much weaker antiferromagnetic interactions are expected from the difference in the crystal structures (stannite versus zinc-blende). A more surprising result is that the exchange constant which controls the AF order below  $T_N$  is *not* between Mn ions with the smallest separation. This result contrasts with a prediction made for the related II-VI DMS, according to which the exchange constants decrease rapidly with distance. [S0163-1829(97)04234-3]

## I. INTRODUCTION

Dilute magnetic semiconductors (DMS's) have been the subject of active research in the last two decades.<sup>1,2</sup> Much of the work has focused on Mn-based II-VI DMS's with zinc-blende or wurtzite crystal structure. A major limitation of these materials arises from the strong antiferromagnetic (AF) interaction between nearest-neighbor (NN) Mn ions, governed by the NN exchange constant  $J_1$ . This  $J_1$  is by far the largest exchange constant. The AF interaction becomes increasingly more important as the Mn concentration  $x$  increases, because a larger percentage of the Mn ions become connected by  $J_1$  bonds. As a result, it is difficult to align the Mn spins when  $x$  is large, even when magnetic fields  $H$  of order 100 kOe are applied at low temperatures. The inability to achieve large magnetizations frustrates attempts to increase the size of magneto-optical effects by increasing  $x$ . The strong NN exchange interaction also limits the achiev-

able binding energies for bound magnetic polarons (BMP's) in II-VI DMS.<sup>3</sup>

Quaternary DMS's with the stannite or wurtz-stannite crystal structures were suggested as a way of avoiding large AF exchange interactions.<sup>4,5</sup> Examples of materials having these structures are discussed in Ref. 6. Figure 1 shows the stannite structure of  $\text{Cu}_2\text{MnSnS}_4$ . In many respects there is a strong similarity to the zinc-blende structure, e.g., each cation is tetrahedrally coordinated to four sulfur anions. However, unlike zinc-blende materials there are three types of cations, with three different valences. The unit cell is therefore doubled in the  $c$  direction. A crucial point is that the three types of cations occupy *ordered positions* in the structure. The Mn ions form a body-centered tetragonal lattice. The minimum distance between two Mn cations is then the lattice constant  $a$ , which is larger than the NN distance  $a/\sqrt{2}$  in the corresponding zinc-blende structure. As a consequence, the exchange interaction which corresponds to the NN exchange constant  $J_1$  in II-VI DMS's is absent. The re-

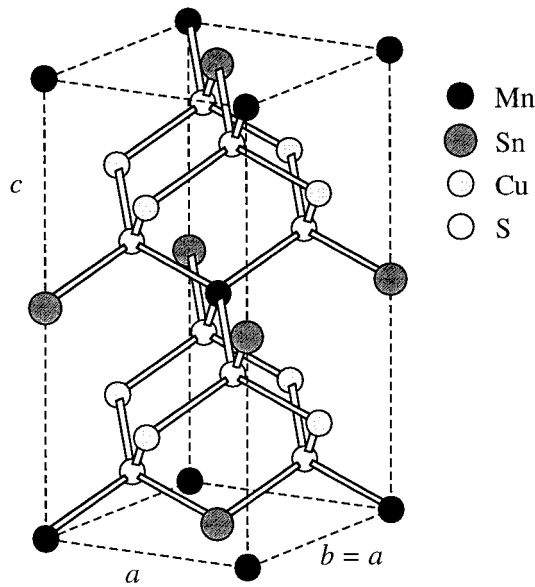


FIG. 1. The stannite structure of  $\text{Cu}_2\text{MnSnS}_4$ .

maining exchange interactions are expected to be smaller by at least one order of magnitude.<sup>7</sup> The absence of  $J_1$  should greatly reduce the overall AF exchange interactions in stannite DMS. A similar reduction of the AF interactions is expected for DMS with the wurtzite-stannite structure. The latter prediction was already confirmed in  $\text{Cu}_2\text{MnGeS}_4$ , which has the wurtz-stannite structure.<sup>8</sup>

Previous works on  $\text{Cu}_2\text{MnSnS}_4$  include the determination of the crystal structure and lattice parameters, and the observation that the material is an antiferromagnet with a Néel temperature  $T_N$  below 20 K (the exact value was not determined).<sup>6,9</sup> Early neutron-diffraction data on a powder<sup>10</sup> suggested that the AF structure is collinear, with a propagation vector  $\mathbf{k}=[1/2,0,1/2]$ , and with the spin axis  $40^\circ$  from the crystallographic  $c$  direction.

In the present paper we present neutron-diffraction and magnetization data on a single crystal of  $\text{Cu}_2\text{MnSnS}_4$ . The neutron data confirm many of the earlier findings,<sup>10</sup> but show that the spin axis is much closer to the  $c$  direction. This conclusion is strongly supported by the magnetization data. Both neutron and magnetic-susceptibility data give a precise value for  $T_N$ . The magnetization data show the characteristic phase transitions of a collinear antiferromagnet: the analog of the spin-flop transition, and the order-disorder transition from the canted phase to the paramagnetic phase. The phase transitions give both the magnetic anisotropy  $K$  and the intersublattice exchange field  $H_E$ . The data confirm the prediction that the AF interactions in the stannite structure are much weaker than in the zinc-blende structure. A related study of the magnetic properties of BMP's in  $\text{Cu}_2\text{Mn}_{0.9}\text{Zn}_{0.1}\text{SnS}_4$  will be published separately.<sup>11</sup>

## II. EXPERIMENT

The single crystal of  $\text{Cu}_2\text{MnSnS}_4$ , with dimensions of about  $3 \times 2 \times 2$  mm, was obtained from a boule grown by the Bridgman method. The crystal had high resistivity at room temperature, and showed none of the magnetic features of BMP's at low temperatures.<sup>11</sup> The high resistivity and ab-

sence of BMP effects indicate that the concentrations of acceptors and/or donors were too low to affect the magnetic behavior.

The neutron-diffraction experiments were performed on the D10 diffractometer of the Institut Laue Langevin, Grenoble (France), in the standard four-circle configuration. The offset Eulerian cradle of this diffractometer is equipped with a helium-flow cryostat operating between 1.6 and 300 K with full four-circle accessibility. All measurements were performed at a constant wavelength of  $1.2593 \text{ \AA}$  obtained from the (200) planes of a copper monochromator and calibrated using a ruby single crystal. The half-wavelength contamination in the incident beam in this configuration is less than  $2 \times 10^{-4}$ . Reflection data corresponding to the nuclear lattice were collected first. A total of 701 reflections were collected at 15.2 K, a temperature which is above but close to the antiferromagnetic transition. Data for analysis of the ordered magnetic phase were taken at 2 K. The temperature dependence of a few selected magnetic reflections was followed in the range from 2 to 12 K. Finally, data from 15 unique reflections were collected at room temperature. The data were analyzed using programs based on the Cambridge Crystallographic Subroutine Library.<sup>12</sup> All data were corrected for background by the minimum  $\sigma(I)/I$  method,<sup>13</sup> and for absorption using a calculated absorption coefficient of  $0.0109 \text{ mm}^{-1}$ . The transmission factors ranged from 0.975 to 0.998.

Magnetization data were obtained with two different magnetometers. Measurements at relatively low magnetic fields,  $H \leq 55$  kOe, were performed with a SQUID magnetometer system manufactured by Quantum Design Inc. This system was operated at temperatures  $1.9 < T < 300$  K. Data at higher fields, up to 300 kOe, were obtained at 1.4 K using a vibrating sample magnetometer which was adapted for use in a hybrid magnet. (A hybrid magnet consists of a Bitter magnet inside a wide-bore superconducting magnet.) Prior to performing the magnetization measurements the sample was oriented using x rays. The angle between the  $c$  axis of the sample and the magnetic field  $\mathbf{H}$  was controlled to better than  $4^\circ$ .

## III. NEUTRON-DIFFRACTION RESULTS

### A. Nuclear structure

The reported tetragonal stannite structure of  $\text{Cu}_2\text{MnSnS}_4$  results from a doubling of the zinc-blende lattice parameters along the  $c$  crystallographic direction. The resulting space group symmetry at room temperature was determined to be  $I\bar{4}2m$  (Ref. 9). In the present work, structural refinement of the atomic positions at 300 K was performed on a limited set of 15 unique reflections. Although the data were limited, the refined crystallographic parameters and atomic positions are in acceptable agreement with the previous determination.<sup>9</sup> The results at 300 K are listed in Table I. The origin of the unit cell has been located at the Mn position.

The crystallographic parameters and atomic positions at 15.2 K, from refinement in space group  $I\bar{4}2m$  against data collected at that temperature, are given in Table II. These results show very good agreement with the proposed structural model. The space group  $I\bar{4}$  which often describes struc-

TABLE I. Atomic coordinates and thermal parameters (temperature factors)  $B$  for  $\text{Cu}_2\text{MnSnS}_4$  at 300 K. (Number of observations: 15 unique reflections. Number of variables: 7. Correlations: less than 70%. Agreement factors:  $wR=0.008$ ,  $\chi^2=3.1$ .) The unit-cell parameters are  $a=5.517(2)$  Å and  $c=10.806(8)$  Å.

Element	$X$	$Y$	$Z$	$B$ (Å <sup>2</sup> )
Cu	0	1/2	1/4	1.7(2)
Mn	0	0	0	2.6(6)
Sn	0	0	1/2	0.6(3)
S	0.252(2)	$X$	0.1314(9)	1.2(5)

tures derived from the zinc blende was also considered as a possibility. The only practical difference between a structural description of  $\text{Cu}_2\text{MnSnS}_4$  in  $I42m$  and in  $I\bar{4}$  is that the positions of the S atoms depend on three parameters ( $X, Y, Z$ ) in  $I\bar{4}$  instead of two ( $X, X, Z$ ) in  $I42m$ . In fact,  $I\bar{4}$  is a subgroup of  $I42m$ . The refinement in the space group  $I\bar{4}$  yielded an agreement factor  $wR=0.025$  and atomic positions for the S atoms [ $X=0.2521(1)$ ,  $Y=0.2521(1)$ , and  $Z=0.13295(6)$ ] matching within experimental uncertainty the positions refined in the  $I42m$  space group. The space group  $I\bar{4}$  was then discarded on the basis of equal values for the  $X$  and  $Y$  coordinates of the S atom and the poorer agreement factor. Thus, the possibility of minor structural changes in the cooling process, which reduce the symmetry of the compound, can be excluded.

### B. Magnetic structure

As the temperature is decreased below approximately 9 K additional diffraction peaks start to develop in rows parallel to half-integer values of reciprocal space axes, while the intensities of the nuclear reflections remain unchanged. Figure 2 shows the positions of the nuclear and magnetic reflections in the  $a^*0c^*$  plane of the reciprocal space. Scans along the main symmetry directions revealed equal intensities for magnetic reflections from four equivalent  $\mathbf{k}$ -propagation vectors:  $[1/2, 0, 1/2]$ ,  $[-1/2, 0, 1/2]$ ,  $[0, 1/2, 1/2]$ , and  $[0, -1/2, 1/2]$ . This situation can correspond either to a collinear structure with propagation vector  $\mathbf{k}=[1/2, 0, 1/2]$  and equal populations of the four  $K$  domains, or to a structure with multi- $\mathbf{k}$  ordering.

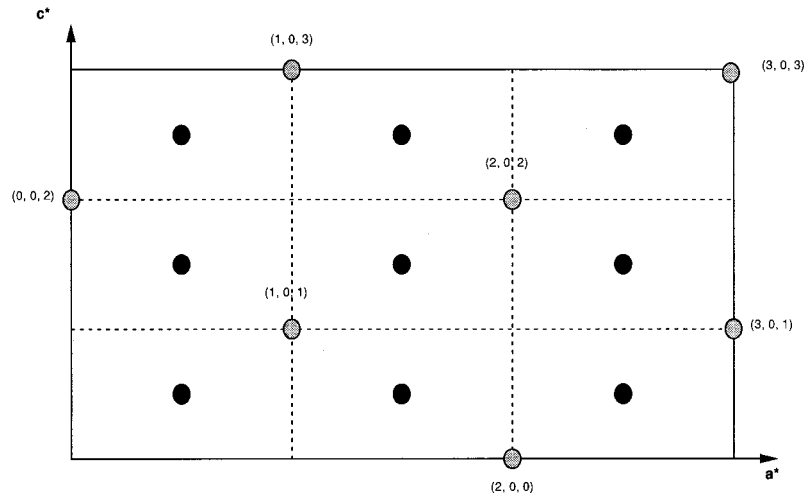


FIG. 2. Reciprocal-space plane showing the scattering points associated with nuclear reflections (shaded circles) and magnetic reflections (filled circles).

TABLE II. Atomic coordinates and thermal parameters for  $\text{Cu}_2\text{MnSnS}_4$  at 15.2 K. (Number of observations: 199 unique reflections. Number of variables: 13. Correlations: less than 70%. Agreement factors:  $wR=0.0155$ ,  $\chi^2=3.38$ . Thermal parameters relate to the expression  $\exp[(-1/4)(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}ha^*kb^* + 2B_{23}kb^*lc^* + 2B_{13}ha^*lc^*)]$ . By symmetry  $B_{22}=B_{11}$  for all atoms and  $B_{13}=B_{23}=B_{12}=0$  for Cu, Mn, and Sn. In the case of S atoms  $B_{13}$ ,  $B_{23}$ , and  $B_{12}$  refine to 0 within the standard deviation.) The unit-cell parameters are  $a=5.514(1)$  Å and  $c=10.789(4)$  Å.

Element	$X$	$Y$	$Z$	$B_{11}$ (Å <sup>2</sup> )	$B_{33}$ (Å <sup>2</sup> )
Cu	0	1/2	1/4	0.220(9)	0.262(12)
Mn	0	0	0	0.340(20)	0.279(31)
Sn	0	0	1/2	0.084(12)	0.126(17)
S	0.25206(10)	$X$	0.13295(8)	0.287(21)	0.252(25)

To distinguish between the two cases in a neutron-diffraction experiment it would be necessary to apply a small external perturbation, such as a magnetic field. The perturbation would modify the balance among the domains in the case of the single- $\mathbf{k}$  structure but would not change the multi- $\mathbf{k}$  structure. Such an experiment was not performed. However, the susceptibility and magnetization measurements reported below are consistent with a collinear structure and exclude multi- $\mathbf{k}$  ordering. The propagation vector  $\mathbf{k}=[1/2, 0, 1/2]$  has also been suggested in an earlier magnetic-structure determination from a powder sample.<sup>10</sup> The resulting magnetic unit cell doubles the nuclear one along the  $a$  and  $c$  crystallographic directions.

The only magnetic atoms in the unit cell are the  $\text{Mn}^{2+}$  ions, since the Cu ions are in the valence state +1 with a closed  $3d$  shell. The wave vector  $\mathbf{k}=[1/2, 0, 1/2]$ , i.e.,  $\mathbf{k}=0.5a^*+0.5c^*=(0.5/a)\hat{a}+(0.5/c)\hat{c}$ , means that the direction of the magnetic moment  $\mathbf{m}$  of a  $\text{Mn}^{2+}$  ion located at  $\mathbf{r}$  is given by

$$\mathbf{m}(\mathbf{r}) = \mathbf{m}(0) \exp(-2\pi i \mathbf{k} \cdot \mathbf{r}). \quad (1)$$

The resulting magnetic structure is represented in Fig. 3.

Values for the magnetic moment of the Mn ion,  $m=4.28(4)\mu_B$ , and for the angle that the moment makes with the  $c$  crystallographic direction,  $\theta=16(2)^\circ$ , have been ob-

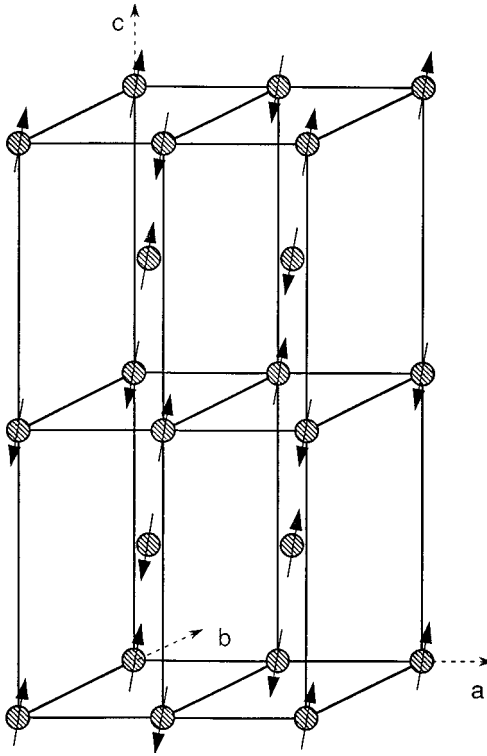


FIG. 3. Orientations of the moments in the magnetic unit cell of  $\text{Cu}_2\text{MnSnS}_4$  for  $\mathbf{k}=[1/2,0,1/2]$ .

tained from a fit to 198 independent magnetic reflections. The program MAGLSQ of CSSL (Ref. 12) was used in this fit with the nuclear parameters fixed to those determined at 15.2 K. The fitting agreement factors were  $wR=0.10$  and  $\chi^2=6.6$ . The value of  $m$  is somewhat lower than the theoretically expected value of  $5\mu_B$  (for a spin  $5/2$  with  $g=2$ ), and is also lower than the value  $m=4.7\mu_B$  obtained from the magnetization data reported below. The difference should be attributed to small electronic transfer to neighboring sulfur atoms due to covalence effects.

The value for the angle  $\theta$  obtained from the fitting is, in fact, less precise than the uncertainty given by the quoted standard deviation. When some low-intensity reflections are excluded from the fit, the value of the moment  $m$  remains unaffected but  $\theta$  can move to any value between  $6^\circ$  and  $16^\circ$ . The value  $16^\circ$  which was quoted above (on the basis of all the measured magnetic reflections) is therefore viewed as an upper limit. This upper limit is still substantially below the value  $\theta=40^\circ$  obtained from the early neutron-diffraction data on a powder.<sup>10</sup> Because  $\theta$  is not zero, the magnetic moment has a component in the basal plane ( $ab$  plane or  $xy$  plane). In the present experiments, symmetry constraints excluded the possibility of determining the orientation of this component in the basal plane.

The orientation of the spin axis does not agree with calculations of the dipole-dipole anisotropy. The dipole-dipole energy for a domain with  $\mathbf{k}=[1/2,0,1/2]$  is minimum when the spin axis is along the  $y$  direction, i.e.,  $\theta=90^\circ$ . Evidently, there are other sources for the anisotropy in this antiferromagnet. As discussed later, the net magnetic anisotropy is quite small.

The temperature dependence of the intensities of some selected magnetic reflections has been followed. Figure 4

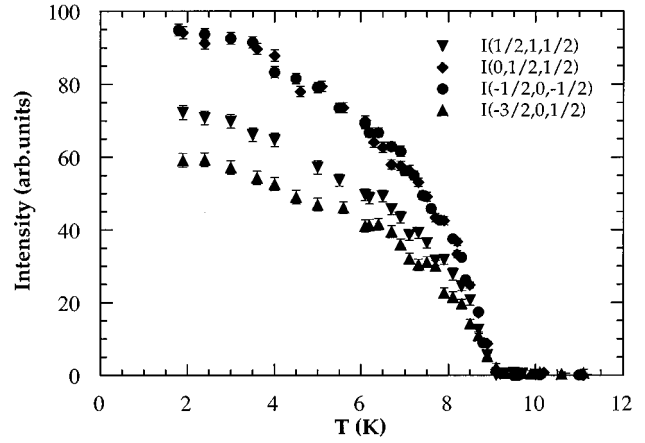


FIG. 4. Temperature dependence of four selected magnetic reflections.

shows the integrated intensities as a function of temperature for the  $(0,1/2,1/2)$ ,  $(1/2,1,1/2)$ ,  $(-1/2,0,-1/2)$ , and  $(-3/2,0,1/2)$  reflections. The intensities of all these reflections, which are purely magnetic, show a sharp rise at the Néel temperature  $T_N=8.8$  K.

## IV. MAGNETIZATION

### A. Low-field susceptibility

The susceptibility  $\chi=M/H$  was measured with the SQUID magnetometer system. Data below 20 K were taken at  $H=1$  kOe with  $\mathbf{H}$  parallel and perpendicular to the  $c$  axis. The results are shown in Fig. 5. The overall behavior agrees with the AF structure deduced from the neutron results, i.e., a collinear AF structure with spin axis close to the  $c$  direction. A well-known example of an ideal collinear AF is  $\text{MnF}_2$ , in which there is a single easy axis parallel to the tetragonal crystallographic direction.<sup>14</sup> The susceptibilities in Fig. 5, for the two field directions, resemble those in  $\text{MnF}_2$  but with two exceptions. First, unlike  $\text{MnF}_2$ , the susceptibility for  $\mathbf{H}\parallel c$  does not approach zero as  $T\rightarrow 0$ . This difference is partially (but not fully) explained by the finite angle  $\theta$  between the  $c$  direction and the spin axis in each of the four  $K$  domains of  $\text{Cu}_2\text{MnSnS}_4$ . The second difference, compared

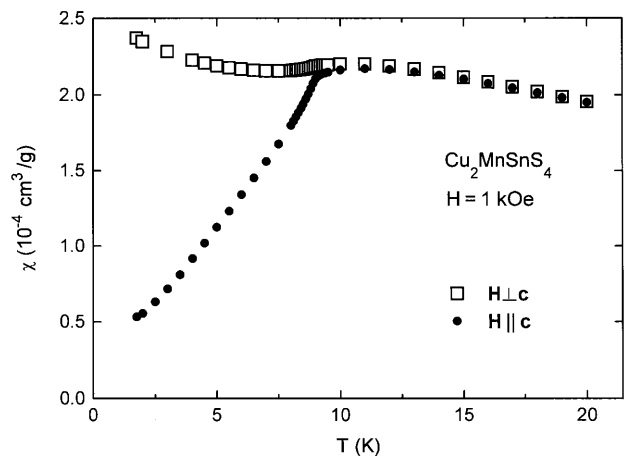


FIG. 5. Temperature dependence of the magnetic susceptibility  $\chi$  (per unit mass) for  $\mathbf{H}$  parallel and perpendicular to the  $c$  axis.

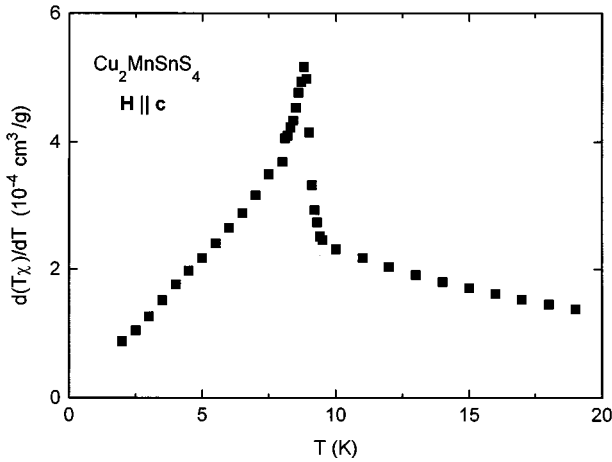


FIG. 6. The derivative  $d(T\chi)/dT$  for  $\mathbf{H}\parallel c$ . These results were obtained numerically from the data in Fig. 5.

to  $\text{MnF}_2$ , is that the susceptibility for  $\mathbf{H}\perp c$  exhibits a small rise below  $T_N$ . Note that at  $T > 10$  K, where the  $\text{Cu}_2\text{MnSnS}_4$  is in the paramagnetic phase, the susceptibility is practically independent of the direction of  $\mathbf{H}$ . This feature is typical for a low-anisotropy antiferromagnet.

Figure 6 shows the derivative  $d(T\chi)/dT$  for  $\mathbf{H}\parallel c$ . These results were obtained numerically from the data in Fig. 5. The  $\lambda$  anomaly exhibited by  $d(T\chi)/dT$  should resemble the anomaly in the specific heat.<sup>15</sup> From the location of the peak in Fig. 6 the Néel temperature is  $T_N = 8.8 \pm 0.1$  K, in agreement with the neutron data. The value of  $T_N$  is only a few percent higher than for  $\text{Cu}_2\text{MnGeS}_4$ .<sup>8</sup>

Susceptibility data for  $T \geq 50$  K and for  $T \geq 100$  K were taken in fields of 25 and 50 kOe, respectively. These fields are “weak” in the sense that  $mH \ll k_B T$ , where  $m$  is the magnetic moment of a  $\text{Mn}^{2+}$  ion and  $k_B$  is the Boltzmann constant. The data for  $1/\chi$  are shown in Fig. 7. They have been corrected for the lattice diamagnetism assuming a lattice susceptibility  $\chi_d = -3 \times 10^{-7}$  emu/g, typical for this type of material.<sup>8</sup> Because the lattice correction is relatively small, the uncertainty in  $\chi_d$  is unimportant. Fits of the data

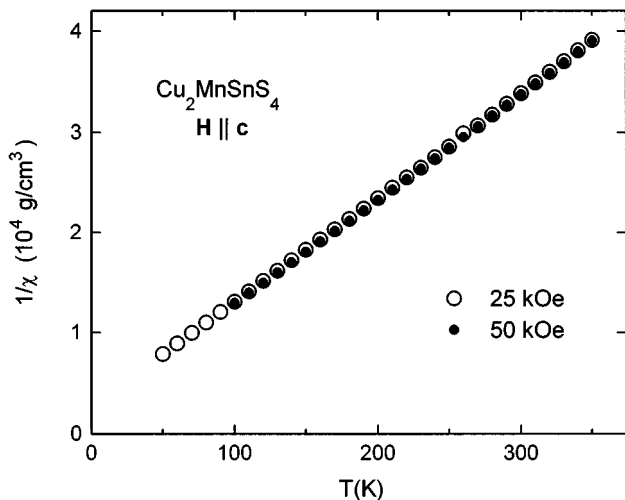


FIG. 7. Temperature dependence of the inverse susceptibility  $1/\chi$  per unit mass. These data have been corrected for the lattice diamagnetism.

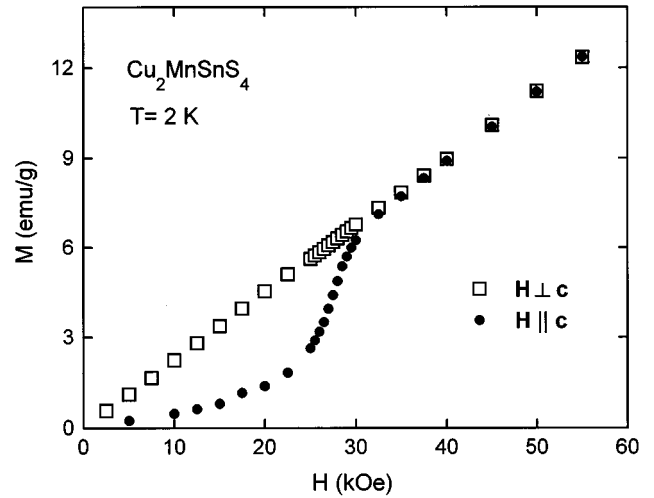


FIG. 8. Field dependence of the magnetization at 2 K, for  $\mathbf{H}$  parallel and perpendicular to the  $c$  axis.

for  $\chi$  vs  $T$  to the Curie-Weiss law gave a Curie constant  $C = (0.96 \pm 0.02) \times 10^{-2}$  cm<sup>3</sup> K/g and a Curie-Weiss temperature  $\Theta = -(25 \pm 2)$  K. The quoted uncertainties include variations introduced by changing the temperature range in the fit, e.g., using only data above 150 K. If one assumes that each  $\text{Mn}^{2+}$  ion has a spin  $S = 5/2$  and a  $g$  factor of 2.00, the theoretical value of  $C$  is  $1.02 \times 10^{-2}$  cm<sup>3</sup> K/g, i.e., 6% above the experimental value. Of greater significance from our perspective is the value of  $\Theta$ . As discussed later, it indicates that the AF interactions in this stannite material have been reduced by more than an order of magnitude relative to a comparable zinc-blende material.

### B. Spin rotation

The spin-flop transition in easy axis antiferromagnets is well known.<sup>14,16–18</sup> This first-order transition occurs when  $\mathbf{H}$  is parallel, or nearly parallel, to the spin axis. At the transition the sublattice magnetizations  $\mathbf{M}_1$  and  $\mathbf{M}_2$  rotate abruptly. The staggered magnetization  $\mathbf{L} = \mathbf{M}_1 - \mathbf{M}_2$  then rotates into a direction perpendicular to  $\mathbf{H}$ . The transition manifests itself as an abrupt increase in the total magnetization  $\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2$ . The magnetic phase above the transition is known as the “spin-flop” phase, or as the “canted” phase (because  $\mathbf{M}_1$  and  $\mathbf{M}_2$  are canted relative to each other in this phase).

When the angle  $\phi$  between  $\mathbf{H}$  and the spin axis exceeds a certain (small) value, the first-order transition disappears.<sup>19</sup> Instead, there is a gradual rotation of  $\mathbf{M}_1$  and  $\mathbf{M}_2$ . Experimentally, the gradual rotation appears as a smeared spin-flop “transition” (see, e.g., Figs. 2 and 3 in Ref. 14). The smearing increases with  $\phi$ . In the present material the spin axis makes a finite angle,  $\theta \leq 16^\circ$ , with the  $c$  direction. Therefore, a smeared spin-flop transition is expected when  $\mathbf{H}$  is parallel to  $c$ .

Magnetization data at 2 K, for  $\mathbf{H}$  parallel and perpendicular to the  $c$  direction, are shown in Fig. 8. These data were obtained with the SQUID magnetometer. The results for  $\mathbf{H}\parallel c$  show the characteristic signature of spin rotation (smeared spin-flop transition). The center of the “transition,” where  $dM/dH$  is maximum, is at 28 kOe. Unlike the results for

$\mathbf{H}\parallel\mathbf{c}$ , the magnetization for  $\mathbf{H}\perp\mathbf{c}$  is nearly proportional to  $H$ . For  $H\geq 35$  kOe the magnetizations for the two field directions are equal. Such equal magnetizations are expected at high fields because for both field configurations ( $\mathbf{H}\parallel\mathbf{c}$  and  $\mathbf{H}\perp\mathbf{c}$ ) the staggered magnetization  $\mathbf{L}$  is perpendicular to  $\mathbf{H}$ . The susceptibility for both field directions is then the perpendicular susceptibility  $\chi_{\perp}$ .

The magnetization curves in Fig. 8 can be used to obtain a certain anisotropy energy. At zero field, the free energy  $G_{AF}$  for the actual spin orientation (with  $\mathbf{L}$  making a small angle  $\theta$  with the  $c$  direction) is lower than the free energy  $G_{SF}$  for the spin-flop configuration with  $\mathbf{L}\perp\mathbf{c}$ . The difference  $K=\Delta G$  is an anisotropy energy. It is given by the area between the two magnetization curves in Fig. 8.<sup>16</sup> Numerical integration gives  $K=6.1\times 10^4$  erg/g. Because the data of Fig. 8 were taken at  $T/T_N<1/4$ , this value for  $K$  should not differ appreciably from that at  $T=0$ . By analogy to the case of an easy-axis antiferromagnet, we define an anisotropy field  $H_A=K/M_S$ , where  $M_S$  is the sublattice magnetization. This gives  $H_A=2$  kOe, which is a fairly low anisotropy field, consistent with the fact that  $\text{Mn}^{2+}$  is an S-state ion. The field  $H_A$  is much smaller than the intersublattice exchange field  $H_E$  discussed below.

### C. Canted-to-paramagnetic transition

At sufficiently high magnetic fields there is an order-disorder transition from the canted phase into the paramagnetic phase.<sup>16-18</sup> The relevant order parameter is the staggered magnetization, which is finite in the canted (ordered) phase but vanishes in the paramagnetic (disordered) phase. In mean-field theory the canted-to-paramagnetic transition is accompanied by a sharp drop in the differential susceptibility  $dM/dH$ . More sophisticated treatments (such as spin-wave theory and modern theory of critical points) lead to a  $\lambda$  singularity in  $dM/dH$ , as discussed in Ref. 18. In three-dimensional materials the  $\lambda$  singularity becomes small at low temperatures,  $T\ll T_N$ . The main feature at the transition is then the large drop in  $dM/dH$ . When the direction of  $\mathbf{H}$  is close to the zero-field spin axis, the transition field  $H_c$  is given by<sup>18</sup>

$$H_c=2H_E-H_A, \quad (2)$$

where  $H_E$  is the intersublattice exchange field. The intrasublattice exchange field does not affect  $H_c$ .<sup>17</sup> In the present case the anisotropy field  $H_A$  is very small compared to  $2H_E$ , so that  $H_c$  is controlled by  $H_E$ . Although all quantities in Eq. (2) are temperature dependent, the changes when  $T/T_N\ll 1$  are small.

Figure 9(a) shows the magnetization curve at 1.4 K in fields up to 300 kOe. These data were obtained in a hybrid magnet using a vibrating sample magnetometer. The relatively fast rise of the magnetization  $M$  near 28 kOe corresponds to the spin rotation in Fig. 8. Following this rise the slope  $dM/dH$  remains nearly constant until the canted-to-paramagnetic transition takes place at high fields. Near 300 kOe the magnetization is practically saturated, at a value of  $61\pm 1$  emu/g. The theoretical saturation value, assuming  $S=5/2$  and  $g=2.00$  for the  $\text{Mn}^{2+}$  ion, is 65 emu/g.

The derivative  $dM/dH$ , obtained numerically from the magnetization curve in Fig. 9(a), is shown in Fig. 9(b). The

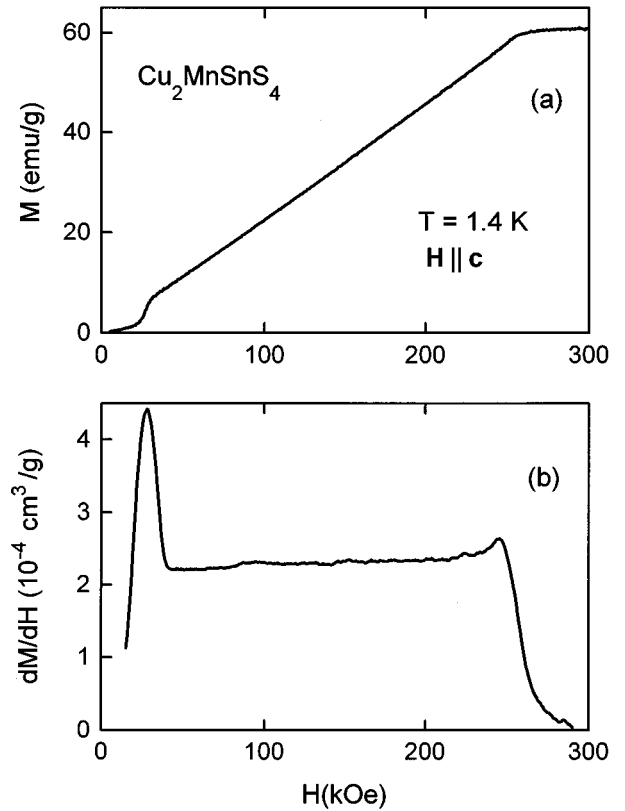


FIG. 9. (a) Magnetization curve at 1.4 K, for  $\mathbf{H}\parallel\mathbf{c}$ . (b) Field dependence of the derivative  $dM/dH$  obtained numerically from the results in (a).

spin rotation near 28 kOe appears as a large peak. The canted-to-paramagnetic transition appears as a small  $\lambda$  peak followed by a large drop. The position of the  $\lambda$  peak, at  $245.5\pm 3$  kOe, is taken as the transition field. Using Eq. (2), with  $H_A=2$  kOe, one then obtains  $H_E=124$  kOe for the intersublattice exchange field. Because this value was obtained at  $T/T_N=0.16$ , it should be close to  $H_E(0)$  at  $T=0$ . The ratio  $\alpha=H_A/H_E=1.6\times 10^{-2}$  is quite low. Both the values of  $H_E$  and  $H_A$  in  $\text{Cu}_2\text{MnSnS}_4$  are comparable to those in  $\text{Cu}_2\text{MnGeS}_4$ .<sup>8</sup>

### V. EXCHANGE INTERACTIONS

To discuss the exchange interactions in  $\text{Cu}_2\text{MnSnS}_4$  we introduce the notation in Fig. 10 for the exchange constants  $J_i$ . This notation is purposely based on the convention for zinc-blende materials. The exchange constant  $J_1$  in the zinc-blende structure is missing in Fig. 10. The reason is that the minimum separation between two Mn ions in the stannite structure is the lattice constant  $a$ , which corresponds to the exchange constant  $J_2$  in the zinc-blende structure. The next two exchange constants,  $J_3$  and  $J_4$ , are for Mn ions separated by  $a\sqrt{3}/2$  and  $a\sqrt{2}$ , respectively, as in the zinc-blende structure. We assume that other exchange constants, for larger separations, can be neglected.

The magnetization data indicate that the AF exchange interactions in  $\text{Cu}_2\text{MnSnS}_4$  are considerably weaker than in a similar material with the zinc-blende structure. The strongest evidence for this conclusion is the Curie-Weiss temperature

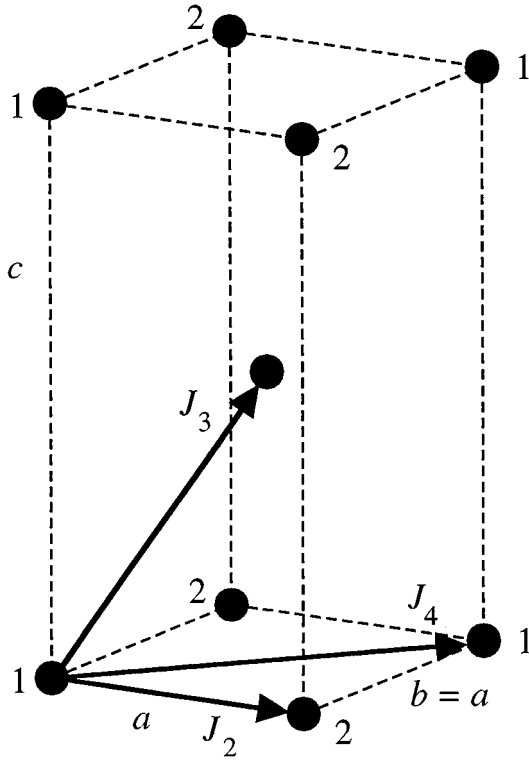


FIG. 10. Notation for the exchange constants  $J_i$  in  $\text{Cu}_2\text{MnSnS}_4$ . This notation is based on the convention for the zinc-blende structure. The closest neighbors in the stannite structure of  $\text{Cu}_2\text{MnSnS}_4$  are separated by a distance which corresponds to the second neighbors in the zinc-blende structure. These closest neighbors are therefore coupled by  $J_2$ . The exchange constant  $J_1$ , for spins separated by  $a/\sqrt{2}$ , does not exist in the stannite structure.

$\Theta$ , which is related to the exchange constants as

$$k_B\Theta = [2S(S+1)/3] \sum z_i J_i. \quad (3)$$

Here,  $z_i$  is the number of neighbors coupled to a given Mn ion by the exchange constant  $J_i$ . In the present material  $\Theta = -25$  K. The corresponding II-VI antiferromagnet is  $\beta\text{-MnS}$  which has two structures, zinc-blende and wurtzite. The  $\Theta$ 's for these structures are  $-982$  and  $-932$  K, respectively.<sup>20</sup> The main reason why  $\Theta$  for  $\text{Cu}_2\text{MnSnS}_4$  is so much lower is that  $J_1$  is absent. A second reason is that there are fewer neighbors connected by  $J_2$ ,  $J_3$ , and  $J_4$  exchange bonds ( $z_2=4$ ,  $z_3=8$ ,  $z_4=4$  for stannite, compared to  $z_2=6$ ,  $z_3=24$ ,  $z_4=12$  for zinc blende).

Another indication that the exchange interactions in  $\text{Cu}_2\text{MnSnS}_4$  are considerably weaker than in II-VI DMS is the lower magnetic field required to saturate the magnetization at low temperatures. Figure 9(a) shows that complete saturation is achieved at 300 kOe. In a comparable II-VI DMS,  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  with  $x=0.25$ , the low-temperature value of  $M$  at 300 kOe is only a third of its saturation value.<sup>21</sup>

A much more surprising result is derived from the AF structure obtained by neutron diffraction. The structure in Fig. 3 implies that the exchange constant  $J_4$ , between Mn ions separated by  $a\sqrt{2}$ , controls the AF order. All four  $J_4$  exchange bonds are satisfied in this structure. In contrast,

only two of the four  $J_2$  exchanged bonds (along the  $\pm a$  directions) are satisfied but the other two  $J_2$  bonds (along the  $\pm b$  directions) are frustrated. On the basis of the current theory for zinc-blende DMS (Refs. 7, 22, and 23) one might have expected that  $J_2$  is one or two orders of magnitude larger than  $J_4$ . If the AF order were governed by  $J_2$ , all four  $J_2$  bonds would have been satisfied and the four  $J_4$  bonds would have been frustrated (i.e., the four Mn spins whose distance from an ‘‘up’’ spin is the lattice constant  $a$  would have had their spins ‘‘down’’). Comparing the actual AF order to hypothetical AF order with  $\mathbf{k}=[1/2,1/2,0]$  in which all  $J_2$  interactions are satisfied, one concludes that  $|J_4|$  must be larger than  $|J_2/2|$ . This conclusion was actually reached earlier,<sup>10</sup> before extensive investigations of DMS had begun. From the present perspective, the important implication is that  $J_i$  need not decrease rapidly with distance, contrary to the common belief among investigators of DMS.

Bruno and Lascaray<sup>24</sup> (BL) have suggested a much weaker distance dependence of the exchange constants  $J_2$  to  $J_4$  than that obtained from the detailed theory.<sup>7,22,23</sup> According to BL,  $J_2$  should be a factor of 4 larger than  $J_4$ . Although the BL argument does not directly apply to the stannite structure, such an argument still suggests that  $J_2$  should exceed  $J_4$  by at least a factor of 2. This prediction is in disagreement with the result  $|J_4| > |J_2/2|$  from the observed AF structure.

There is some evidence that even in some II-VI DMS's the exchange constant  $J_2$  may not be larger than both  $J_3$  and  $J_4$ . Recent magnetization-step data<sup>25</sup> suggest that in some Mn-based II-VI DMS, either  $J_3$  or  $J_4$  is larger than  $J_2$ . If these results are confirmed, then the present theory for the exchange interactions between distant neighbors in II-VI DMS will have to be modified.

More quantitative information about the exchange constants in  $\text{Cu}_2\text{MnSnS}_4$  can be obtained using  $\Theta$  and  $H_E$ . From Eq. (3), with  $S=5/2$ ,

$$k_B\Theta = (70/3)(J_2 + 2J_3 + J_4). \quad (4)$$

The *intersublattice* exchange field  $H_E$  is related to the exchange constants as

$$g\mu_B H_E = -2S \sum z'_i J_i, \quad (5)$$

where  $z'_i$  is the number of neighbors *on the opposite sublattice* which are coupled to a given Mn ion by the exchange constant  $J_i$ . For the present AF structure,  $z'_2=2$ ,  $z'_3=4$ , and  $z'_4=4$ , so that

$$g\mu_B H_E = -10(J_2 + 2J_3 + 2J_4). \quad (6)$$

Using the experimental results for  $\Theta$  and  $H_E$ , and setting  $g=2.00$ , one then obtains  $J_4/k_B \cong -0.6$  K, and  $(J_2 + 2J_3)/k_B \cong -0.5$  K.

Additional support for these values is obtained from the observed  $T_N$ . In mean-field theory for the present AF structure,

$$k_B T_N = -4J_4 [2S(S+1)/3]. \quad (7)$$



Going beyond mean-field theory one typically has to multiply the right-hand side of Eq. (7) by a factor of about 0.7, assuming three-dimensional order.<sup>18</sup> From  $T_N=8.8$  K one then obtains  $J_4/k_B \cong -0.5$  K, which is close to the estimate from  $\Theta$  and  $H_E$ . The values for all the exchange constants in  $\text{Cu}_2\text{MnSnS}_4$  are small compared to  $J_1$  in II-VI DMS's, typically  $J_1/k_B \cong -10$  K.<sup>7,26</sup> The weak exchange interactions in the stannite structure confirm the prediction of Wolff and Ram-Mohan<sup>4</sup> and Heiman *et al.*<sup>5</sup>

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