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Neutron diffraction study of the magnetic structures of $CeMn_2Ge_2$ and $CeMn_2Si_2$

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We have performed high-resolution neutron powder diffraction measurements on $CeMn_2Si_2$ and $CeMn_2Ge_2$ at temperatures between 12 and 550 K. Our measurements indicate that at high temperatures both compounds are paramagnetic. Below $T_N=380$ K $CeMn_2Si_2$ becomes a collinear AF, with a structure similar to that reported by Siek *et al.* in which the magnetic propagation vector is $\tau=(0\ 0\ 1)$. $CeMn_2Ge_2$, on the other hand, exhibits two different magnetic transitions. At $T_N\approx415$ K there is a transition to a collinear AF phase characterized by the commensurate propagation wave vector $\tau=(1\ 0\ 1)$. At $T_C\approx318$ K there is a transition to a conical structure with a ferromagnetic component along the *c* axis and a helical component in the *ab* plane. The helical component is characterized by the incommensurate propagation vector $\tau=(1\ 0\ 1-q_z)$, where q_z is temperature dependent. © *1996 American Institute of Physics.* [S0021-8979(96)73208-8]

INTRODUCTION

The family of layered compounds of the form RM_2X_2 (R=rare earth, M=transition metal, X=Si, Ge) crystallizes with the $ThCr_2Si_2$ ($I4/mmm$) structure and exhibits a rich variety of interesting physical phenomena that include superconductivity, magnetism, mixed valence, heavy fermion or Kondo behavior. Of particular interest is the system $CeMn_2X_2$, which exhibits magnetic moments only at the Mn sites. In this system the Mn atoms form a simple tetragonal lattice and are coupled with an exchange interaction that has been thought to be sensitive to the Mn-Mn distances within (0 0 1) planes (intralayer exchange) and relatively insensitive to the Mn-Mn distances along the *c* axis (interlayer exchange). It has been reported that the Mn moments in $CeMn_2Si_2$ are aligned ferromagnetically within the (0 0 1) planes, and that these planes are coupled antiferromagnetically below $T_N=379$ K.[1] The $CeMn_2Ge_2$ system, on the other hand, has been reported to be ferromagnetic (FM) below $T_C=316$ K.[2,3] Recently Venturini *et al.*[4] have reported that in the related compounds $LaMn_2Si_2$ and $LaMn_2Ge_2$ there is strong evidence of dominant intralayer antiferromagnetic interactions, which give rise to conical incommensurate phases at low temperatures. These results suggest that the nature of the magnetic interactions in this family of compounds is more complex than originally thought, and that the magnetic structures of $CeMn_2Si_2$ and $CeMn_2Ge_2$ should be reexamined. We have performed high-resolution neutron powder diffraction measurements on these compounds to resolve the magnetic structures and the nature of the magnetic interactions in these systems. In this article we report the findings of our preliminary analysis of these measurements. We found that at high temperatures both compounds are paramagnetic. $CeMn_2Si_2$ becomes a collinear antiferromagnet below $T_N\approx380$ K, with a structure similar to that reported by Siek *et al.*,[1] in which the magnetic propagation vector is $\tau=(0\ 0\ 1)$. Below $T_N\approx415$ K $CeMn_2Ge_2$ is a collinear antiferromagnet with a commensurate propagation wave vector $\tau=(1\ 0\ 1)$. Below $T_C\approx318$ K the Mn moments in this system exhibit a conical structure with a ferromagnetic component along the *c* axis and a helical component in the *ab* plane, similar to that of $LaMn_2Ge_2$ reported by Venturini *et al.*[4] This helical component is characterized by the incommensurate propagation vector $\tau=(1\ 0\ 1-q_z)$, where q_z is temperature dependent and varies from 0 (at T_C) to 0.32 reciprocal lattice units (at $T=12$ K). These findings are consistent with the recent results reported by Welter *et al.*[5]

EXPERIMENT

About 10 g of $CeMn_2Ge_2$ and $CeMn_2Si_2$ were prepared by arc melting stoichiometric amounts of the constituents in an argon atmosphere. X-ray diffraction analysis showed that these specimens had no significant amounts of impurity phases. The samples were powdered and loaded in thin-walled aluminum or vanadium cells for the neutron diffraction measurements. For the measurements between 12 and 330 K the cells were sealed in a He gas environment, and then placed in a closed cycle He refrigerator. For the high temperature measurements (330 K$<T<$550 K) the cells were placed in a furnace. The neutron diffraction measurements were performed at the HB4 high-resolution powder diffractometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory using neutron wavelengths of 1.417 and 2.222 Å.

$CeMn_2Si_2$

Powder diffraction patterns of $CeMn_2Si_2$ were collected between 12 and 430 K. At 430 K there was no evidence of any magnetic contribution to the diffraction pattern, and the crystal structure at this temperature was refined using the computer program RIETAN.[6] The refined structural param-

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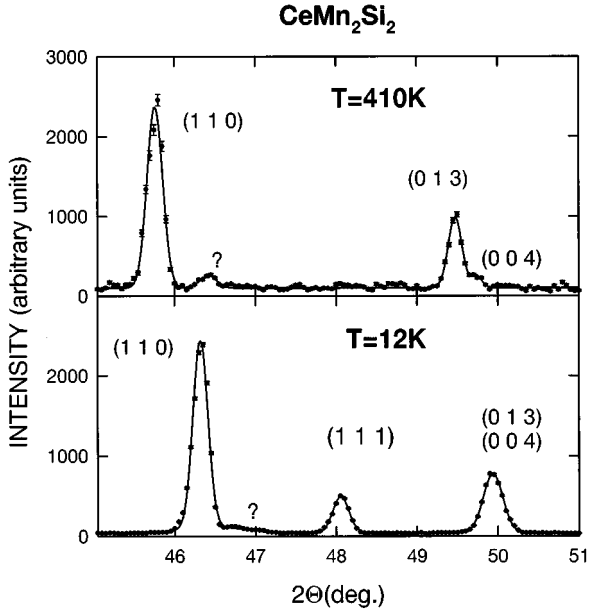

FIG. 1. Partial neutron powder diffraction pattern for $CeMn_2Si_2$ at $T=410$ K and 12 K. The low temperature (1 1 1) peak is of magnetic origin and is indicative of an antiferromagnetic structure with a characteristic propagation wavevector $\tau=(0\ 0\ 1)$ (see text). The solid lines are the result of fits to Gaussian lineshapes. The peak labeled with a question mark corresponds to an unidentified impurity phase. The neutron wavelength for this measurement was $\lambda=2.22$ Å.

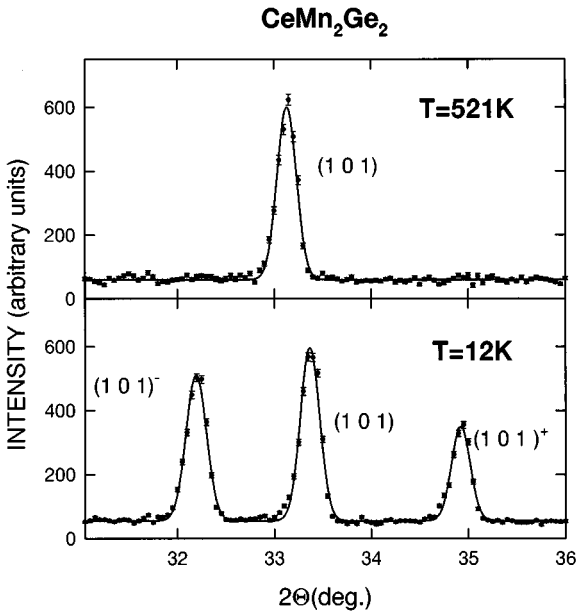

FIG. 2. Partial neutron powder diffraction pattern for $CeMn_2Ge_2$ at $T=521$ K and 12 K. The low temperature magnetic satellites in the vicinity of the (1 0 1) peak are of magnetic origin and are indicative of a helical component of the Mn magnetic moments with characteristic propagation wavevector $\tau=(1\ 0\ 1-q_z)$. The neutron wavelength for this measurement was $\lambda=2.22$ Å.

eters are consistent with the published values for this material with the Ce, Mn, and Si atoms at the 2(a), 4(d) and 4(e) sites of the space group $I4/mmm$, $a=4.0417(6)$ Å, $c=10.5546(19)$ Å, and $z=0.382(1)$ (where z is the variable fractional coordinate of the Si atoms). In this space group the nuclear reflection conditions for (hkl) are $h+k+l=2n$. An extra reflection condition, $l=2n$, exists for the scattering contribution from the Mn sites. As the temperature was lowered two superlattice peaks were observed. These could be indexed as the (1 1 1) (see Fig. 1) and the (1 1 3) reflections. These superlattice peaks appeared below $T_N\approx380$ K and persisted all the way down to 12 K. These findings are similar to those reported by Siek *et al.*[1] and correspond to an antiferromagnetic structure with a propagation vector $\tau=(0\ 0\ 1)$. The absence of reflections of the form $(0\ 0\ 2n\pm1)$ indicates that the magnetic moments are parallel to the c axis. In this collinear antiferromagnetic structure the magnetic moment M_z at the Mn site $\mathbf{r}_1$ is

$$M_z(\mathbf{r}_1)=M_0\cos(\mathbf{r}_1\cdot\tau), \tag{1}$$

where τ is the propagation vector characteristic of the magnetic structure in reciprocal lattice units, and M_0 is the magnitude of the magnetic moment. Thus in this structure all the Mn moments in the (0 0 1) planes are coupled ferromagnetically, while the moments in adjacent (0 0 1) planes are coupled antiferromagnetically. The magnetic moment per Mn atom at 12 K was calculated from the integrated intensities of the (1 1 1) magnetic peak and the (1 1 0) nuclear peak shown in Fig. 1. In this calculation a small correction (<5%) was made to account for the preferred orientation present in the powder. The calculated moment was of 1.9(2) μ_B per Mn atom. This value is lower than the value 2.30(5) μ_B reported by Siek *et al.*[1] and lower than the paramagnetic moment of 3.3 μ_B reported by Liang *et al.*[7] At $T=12$ K the refined structural parameters were $a=3.9913(4)$ Å, $c=10.4935(13)$ Å, and $z=0.3805(8)$.

$CeMn_2Ge_2$

Powder diffraction patterns of $CeMn_2Ge_2$ were collected between 12 and 550 K. At 550 K there was no evidence of any magnetic contribution to the diffraction pattern, and the crystal structure at this temperature was refined using the computer program RIETAN.[6] This structure is similar to that of $CeMn_2Si_2$, with the Ce, Mn, and Ge atoms at the 2(a), 4(d) and 4(e) sites of the space group $I4/mmm$, the refined structural parameter at 521 K were $a=4.1623(3)$ Å, $c=11.0081(9)$ Å, and $z=0.3832(5)$ (where z is the variable fractional coordinate of the Ge atoms). As the temperature was lowered we found evidence of two magnetic transitions. Below $T_N\approx415$ K the intensity of the (1 0 1) reflection increased, reaching a maximum at about $T=320$ K and then dropped rapidly to the same level of the high temperature patterns. Below $T_C\approx318$ K magnetic satellites appeared in the vicinity of the (1 0 1) (see Fig. 2), (1 0 3), (1 0 5), (2 1 1), and (2 1 3) reflections, at the same time that the intensity of the (1 1 0), (1 1 2), (1 1 4) and (2 0 2) peaks increased. The intensities of the reflections (0 0 2n) remained unchanged in the whole temperature range studied. These observations are consistent with the existence of two different magnetic phases in $CeMn_2Ge_2$.

The enhancement of the (1 0 1) reflection below T_N could originate either by the appearance of ferromagnetic

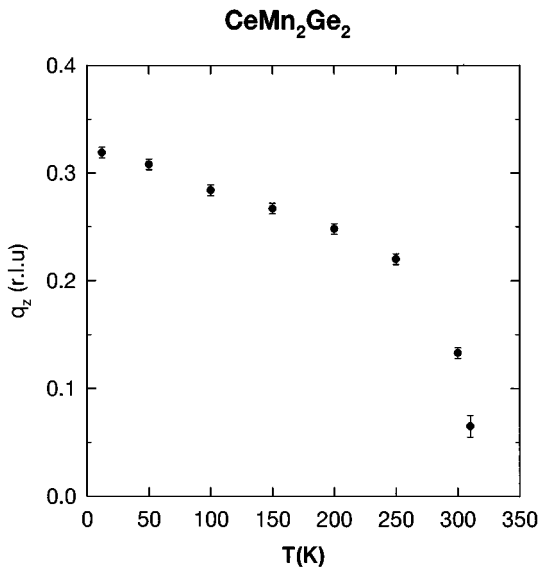

FIG. 3. Temperature dependence of q_z for $CeMn_2Ge_2$. q_z is given in reciprocal lattice units (r.l.u).

ordering of the Ce atoms, or by the appearance of antiferromagnetic ordering of the Mn atoms (i.e., by the formation of a superlattice of Mn atoms). The magnetic ordering of the Ce atoms, however, would also increase the intensity of most of the allowed nuclear reflections. This intensity enhancement has not been observed, indicating that no magnetic ordering is associated with the Ce atoms. This observation is consistent with earlier reports that Ce is nonmagnetic in this family of compounds.[8,9] Other Lanthanides in RMn_2X_2 systems exhibit magnetic order but at much lower temperatures.[8] The enhancement of the (1 0 1) reflection can then be attributed to the antiferromagnetic ordering of the Mn atoms with a characteristic propagation wave vector $\tau=(1\ 0\ 1)$. As in the case of $CeMn_2Si_2$ the direction of the magnetic moments is parallel to the c axis. Unlike the $CeMn_2Si_2$ system both the intralayer and interlayer couplings of the Mn moments are antiferromagnetic, their directions given by Eq. (1).

The enhancement of the (1 1 0), (1 1 2), (1 1 4) and (2 0 2) peaks below $T_C \approx 318$ K can be attributed to the development of a ferromagnetic alignment of the Mn moments. The appearance of magnetic satellites at the same temperature can be attributed to the simultaneous appearance of a helical component of the Mn moments in the *ab* plane, with a characteristic wave vector $\tau=(1\ 0\ 1-q_z)$. The value of q_z is incommensurate with the lattice and is temperature dependent (see Fig. 3), varying from 0 (at T_c) to ≈ 0.32 (at 12 K). In this structure the M_x, M_y, and M_z components of the magnetic moment $\mathbf{M}(\mathbf{r}_1)$ are given by

$$M_x(\mathbf{r}_1)=M_0\ \cos(\mathbf{r}_1\cdot\tau+\phi),$$
$$M_y(\mathbf{r}_1)=M_0\ \sin(\mathbf{r}_1\cdot\tau+\phi),\quad M_z(\mathbf{r}_1)=M_1. \tag{2}$$

These components result in a conical structure similar to that described by Venturini *et al.* for $LaMn_2Ge_2$.[4] The refined ferromagnetic component M_z for Mn at $T=12$ K was $2.4(2)\mu_B$. The refined structural parameters at this temperature were $a=4.1291(2)$ Å, $c=10.9016(7)$ Å, and $z=0.3820(4)$.

DISCUSSION

The nature of the magnetic interactions in the systems under study is more complex than originally thought. The short distance between the Mn nearest neighbors ($a\sqrt{2}/2$) is suggestive of strong direct exchange interactions between the magnetic ions. The relatively large distance ($c/2$) between the Mn (0 0 1) planes suggests indirect exchange interactions mediated by the Ge/Si and Ce atoms. For $CeMn_2Si_2$ the intralayer exchange interaction between Mn moments is ferromagnetic, while the interlayer is antiferromagnetic. For $CeMn_2Ge_2$ on the other hand, the intralayer exchange is antiferromagnetic, while the interlayer is such that gives rise to a transition from a commensurate antiferromagnetic phase to an incommensurate conical structure. The nature of this commensurate-to-incommensurate phase transition, which takes place with a magnetic moment reorientation is of special interest and should be studied further. Recent bulk magnetization measurements on a specimen of $CeMn_2Ge_2$ (from the same batch as our sample) revealed an anomaly in the magnetization at the same temperature where this spin reorientation takes place.[10] When this work was in progress we learned of the recent published results of Welter *et al.*[5] on $CeMn_2Ge_2$; our results on this system are in general agreement with theirs. Our results are also in general agreement with the recent Mössbauer experiments by Nowick *et al.*[11]

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