There has been a recent resurgence of interest in narrow band ferromagnetism, due to the discovery of a possible connection between superconductivity and the ferromagnetic quantum critical point.\textsuperscript{1,2} CeGe\textsubscript{2} is an example of a narrow band ferromagnet, which was first reported by Matthias\textsuperscript{3} as ordering at $T_C = 4.5$ K, and crystallizes in an orthorhombically distorted tetragonal ThSi\textsubscript{2}-type structure. Later, several groups\textsuperscript{4-8} confirmed the crystal structure and ferromagnetic state but showed the magnetic phase transition occurs at $T_C = 7$ K. It was also shown\textsuperscript{6-8} that the crystal structure and $T_C$ are almost unchanged by introducing low concentrations of Ge vacancies (CeGe\textsubscript{x} with 1.6<x<2.0). For a sample with a Ge concentration close to $x = 1.6$, the structure is the tetragonal ThSi\textsubscript{2} phase, and $T_C$ occurs at about 6 K. Mori \textit{et al.}\textsuperscript{5} studied the (Ce\textsubscript{1-x}La\textsubscript{x})Ge\textsubscript{2} system and suggested that CeGe\textsubscript{2} is a Kondo system with $T_K = 2.7$ K. Most of the Ce based magnetically ordered compounds have been classified\textsuperscript{9} according to their Ce–Ce spacing ($D$). It is found that Ce based compounds having the $D$ values ranging between 3.7 and 4.1 Å order ferromagnetically and those having $D > 4.1$ Å order antiferromagnetically. CeGe\textsubscript{2} has the minimum Ce–Ce spacing $D = 4.12$ Å and was classified as the only ferromagnet with $D > 4.1$ Å. We have further investigated the temperature and magnetic field dependence of the specific heat and magnetization for the CeGe\textsubscript{2} system and surprisingly found that our data are dramatically different from previously published results. Our data show that CeGe\textsubscript{2} exhibits two magnetic transitions: an antiferromagnetic transition at $T_N = 7$ K and a ferromagnetic transition at $T_C = 4.3$ K. $T_C$ increases with increasing applied field while $T_N$ decreases only slightly. These two magnetic transitions merge to become a single ferromagnetic transition at applied fields equal to or larger than 5 kG. We have also observed similar magnetic transitions for low concentrations of Ge vacancies in CeGe\textsubscript{x}.

Polycrystalline CeGe\textsubscript{2} samples were prepared in an inert atmosphere arc furnace with appropriate care taken to compensate for the weight loss of the more volatile Ge. The samples were wrapped in Ta foils and annealed under vacuum at 800 °C for time intervals ranging from 3 days to 2 weeks. Room temperature powdered x-ray diffraction measurements indicate that all the samples, with different annealing times, were single phase. The crystal structure is an orthorhombically distorted ThSi\textsubscript{2} tetragonal phase with the measured lattice parameters, $a = 4.28$ Å, $b = 4.32$ Å, $c = 14.08$ Å, which are consistent with those previously published.\textsuperscript{3-5} The magnetization was measured from 2 to 300 K in magnetic fields up to 55 kG. The specific heat was measured using the semiadiabatic heat pulse method from 1.2 to 30 K in magnetic fields up to 35 kG.

Figure 1 shows the temperature dependence of the magnetization $M(T)$ measured at an applied magnetic field of 100 G for CeGe\textsubscript{2}. The zero-field-cooled (ZFC) and field-cooled (FC) data are essentially identical except below 3 K the ZFC data saturate and the FC data increase monotonically with decreasing temperature. One can see that a cusp occurs at 7 K. This cusp feature together with the linear dependence of the magnetization $M(H)$ measured in low applied fields ($H < 2$ kG) at $5 K \leq T \leq 7$ K (Fig. 3) indicate that CeGe\textsubscript{2} undergoes an antiferromagnetic transition at $T_N = 7$ K. As the temperature is lowered, the magnetization increases rapidly below 5 K indicating a second transition to a ferromagnetic state. The Curie temperature $T_C$, defined at the temperature where the maximum value of $\left| dM/dT \right|$ occurs, is 4.3 K for CeGe\textsubscript{2}. As mentioned earlier, all the previous observations reported a single ferromagnetic transition in CeGe\textsubscript{2}. This is the first observation of antiferromagnetic ordering and the existence of two magnetic transitions for this compound.

A plot of the inverse magnetic susceptibility versus temperature at high temperatures (inset of Fig. 1) indicates a Curie–Weiss behavior, i.e., $\chi = C/(T - \theta)$. The effective paramagnetic moment deduced from the Curie constant is $\mu_{\text{eff}} = 2.38 \mu_B$ consistent with the previously reported values.\textsuperscript{4,5} This $\mu_{\text{eff}}$ value is close to 2.54 $\mu_B$, which is ex-
pected for trivalent Ce ions. The value of $\theta$ is close to zero, for all of the samples investigated. This is consistent with CeGe$_2$ being a magnetically frustrated system. It is interesting to note that the magnetic susceptibility $\chi=0.380$ emu/mol G at $T_\text{N}$ measured in low fields, i.e., $H<2.0$ kG, is an order of magnitude larger than those of other Ce based antiferromagnetic compounds.$^{10-12}$

The temperature dependence of the magnetization data $M(T)$ for CeGe$_2$ is shown in Fig. 2 for high applied fields. $T_C$ seems to increase with increasing applied field initially and becomes unclear at high fields because the ferromagnetic transition broadens. $T_N$ can be easier to determine and is only slightly lowered with increasing magnetic field. For example, $T_N$ is 6.8 K at $H=2$ kG and 6.6 K at $H=3$ kG. $M(T)$ measured at $H=4$ kG shows a kink in the vicinity of 6.5 K. These two magnetic transitions merge to become a single ferromagnetic transition at higher fields, i.e., $H>5$ kOe.

The field dependence of the magnetization data $M(H)$ of CeGe$_2$ is shown in Fig. 3 for $2 \text{ K} < T \leq 8$ K. It can be seen that below $H=2.0$ kG the magnetization measured at 6 K, which is below the first magnetic transition, increases linearly with increasing field. This linear behavior together with the cusp feature shown in Fig. 1 lead to the conclusion that CeGe$_2$ undergoes an antiferromagnetic transition at $T_N=7$ K. On the contrary, the magnetization data measured at $T=2$ K and 4 K increase very rapidly at very low fields, e.g., $H<200$ G. This observation, which is consistent with the temperature dependence of the magnetization $M(T)$, indicates that ferromagnetism occurs below $T_C=4.3$ K. $M(H)$ at $T=2$ and 4 K increases more rapidly again for $H>2$ kG and then increases slowly for $H>6$ kG. This behavior is typical for ferromagnets with strong anisotropy. $M(H)$ at 6 K starts to deviate from linearity and increases more rapidly for $H>2.0$ kG. This agrees with the conclusion, drawn from the temperature dependence of the magnetization at different fields, that $T_C$ and $T_N$ merge at high fields and CeGe$_2$ exists in a ferromagnetic state.

At $T=2$ K, the magnetic moment is not saturated in an applied field of 55 kG (not shown), and is 0.97 $\mu_B$/Ce atom.

Mori et al.$^5$ have measured the magnetization for CeGe$_2$ in pulsed fields up to 400 kG at 4.2 K. Their results showed that the magnetic moment is 1.4 $\mu_B$/Ce atom at $H=400$ kG and has not completely saturated. For comparison, Lambert-Andron et al.$^6,7$ have carried out neutron experiments on a single crystal of CeGe$_{1.6}$ which exhibits a single ferromagnetic transition at $T_C=6$ K and crystallizes in the tetragonal structure (no distortion). Their results showed that the spontaneous ferromagnetic moment is 1.5 $\mu_B$/Ce atom oriented along the c axis.

Figure 4 shows the $C/T$ vs $T$ data of CeGe$_2$ measured at $H=0$, 10, and 35 kG. It can be seen clearly that at $H=0$, two specific heat anomalies occur at about 7 and 4.3 K. Since specific heat is a bulk effect, the data at $H=0$ confirm the two magnetic transitions in CeGe$_2$. The $C/T$ data of CeGe$_2$ measured at $H=10$ kG show a broad maximum and almost merge with the data in $H=0$ at $T=12$ K. It was mentioned from the magnetization measurements that $T_C$ increases with

\[ \text{FIG. 1. The magnetization } M(T) \text{ of CeGe}_2 \text{ measured at } H=100 \text{ G. Inset: the inverse of magnetic susceptibility } (1/\chi) \text{ vs } T. \]

\[ \text{FIG. 2. The temperature dependence of the magnetization } M(T) \text{ of CeGe}_2 \text{ measured at } H=1, 2, 3, 4, \text{ and } 5 \text{ kG.} \]

\[ \text{FIG. 3. The magnetic field dependence of the magnetization } M(H) \text{ of CeGe}_2 \text{ measured at } T=2, 4, 5, 6, 7, \text{ and } 8 \text{ K.} \]
increasing applied field and merges with $T_N$ at a field of 5 kG, and therefore the specific heat anomaly at about 4.3 K in $H=0$ disappears at $H=10$ kG. The data measured at $H=35$ kG exhibit an even broader maximum which is characteristic of ferromagnetism.

Figure 5 shows the $C/T$ vs $T^2$ data at $H=0$ from $T=1.2$ to 20 K. The $C/T$ vs $T^2$ data are essentially linear for $T>10$ K. $\gamma_{HT}$ is defined as the value of the intercept to the $C/T$ axis from the extrapolation of the linear fit (i.e., $C/T = \gamma + \beta T^2$) at high temperatures, and is 120 mJ/mole K$^2$ for CeGe$_2$. The $\beta$ value obtained from the above fit is 0.620 mJ/mol K$^4$. The Debye temperature can then be deduced from the $\beta$ value and is 210 K. Although $\gamma_{HT}$ of CeGe$_2$ is not as large as the $\gamma$ values at $T=0$ of nonmagnetic heavy fermion materials, it is enhanced and is comparable to the $\gamma_{HT}$ values of Ce based Kondo and heavy fermion systems. The magnetic entropy removal ($\Delta S$) can be calculated by integrating the $C_{\text{mag}}/T$ vs $T$ data, where $C_{\text{mag}}-C_{\text{total}}-(\gamma_{HT}T + \beta T^2)$. $\Delta S$ is 4.36 J/mol K at $H=0$ up to $T=7$ K. This is about 76% of $R \ln 2 (5.75$ J/mol K) expected for the doublet ground state of trivalent Ce ions.

A useful relation between $\chi$ and $\gamma$ is the “Wilson ratio” $R = \{(\pi^2 k^2)/[g^2 J(J+1)\mu_B]^2\}[\chi(T=0)/\gamma]$. The Wilson ratio is about $R=1$ for nonmagnetic heavy fermion systems. The $\chi(T=0)$ value cannot be determined for magnetic systems and the Wilson ratio is estimated from $\chi(T)$ just above $T_N$ for antiferromagnetic systems. If $\chi$ at $T=10$ K is used, which is well above $T_N$, and $\gamma$ is taken as $\gamma_{HT}$ for CeGe$_2$, then $R$ is about 32 which is surprisingly large. The $R$ value is even much larger if the $\chi$ value is taken at $T_N=7$ K. This ratio is much larger than those of Ce and U based magnetic heavy fermion systems. The very large Wilson ratio is generally indicative of a ferromagnetic state. In fact, CeGe$_2$ exhibits two magnetic transitions with an antiferromagnetic transition at 7 K and a ferromagnetic transition at 4.3 K, and becomes a single ferromagnetic state in an applied field of 5 kG. This, together with the very small $\theta$ value found for the high temperature magnetic susceptibility data fit to a Curie–Weiss law $[\chi=C/(T-\theta)]$, show that CeGe$_2$ is close to the instability of ferromagnetic and antiferromagnetic ordering.

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**References**


