

## Antiferromagnetic order in pure CeFe<sub>2</sub> under pressure

D. Braithwaite, G. Lapertot, and B. Salce

*Département de Recherche Fondamentale sur la Matière Condensée, SPSMS, CEA-Grenoble, 38054 Grenoble, France*

A.-M. Cumberlidge and P. L. Alireza

*Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom*

(Received 27 September 2007; published 26 December 2007)

The low temperature and high pressure ferromagnetic and antiferromagnetic phases of pure single crystals of CeFe<sub>2</sub> and cobalt doped Ce(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub> are studied by ac susceptibility measurements. We find that in the cobalt doped system, the low temperature antiferromagnetic phase is reinforced by the application of pressure. In pure CeFe<sub>2</sub>, a probable switch to an antiferromagnetic ground state at low temperature occurs at a pressure of less than 2 GPa, and the ferromagnetic state is completely replaced at a pressure of about 6 GPa. This ground state is discussed in light of previous experiments on the cobalt and aluminum doped systems.

DOI: [10.1103/PhysRevB.76.224427](https://doi.org/10.1103/PhysRevB.76.224427)

PACS number(s): 75.30.Kz

### I. INTRODUCTION

Among the cubic Laves phase ferromagnets of the RFe<sub>2</sub> (R=rare earth) family, CeFe<sub>2</sub> is an exception, showing an abnormally low Curie temperature (230 K) and reduced saturation moment ( $M_S=2.3\mu_B$ ), both attributed to the strong hybridization of the Ce valence bands with the Fe 3d electrons.<sup>1</sup> Inelastic neutron scattering reveals a coexistence of antiferromagnetic (AFM) fluctuations in the ferromagnetic (FM) ground state,<sup>2</sup> indicating that the system is close to an AFM instability. Furthermore, doping CeFe<sub>2</sub> with a small amount of various materials (Co and Al) produces an AFM ground state. Many studies have been devoted to the quantum phase transition between an AFM state and a paramagnetic state in cerium compounds, but so far, little attention has been paid to quantum effects related to transitions between other kinds of states. Thus, this system might provide a nice example to study the quantum phase transition between a FM and an AFM ground state at low temperature. In this study, we show that it is also possible to achieve the AFM ground state through the application of a pressure of about 2 GPa on pure CeFe<sub>2</sub>, opening the possibility to study the transition in very clean samples, whereas the doped samples are inevitably somewhat disordered. Several previous studies hinted that high pressure might be able to stabilize the AFM ground state in pure CeFe<sub>2</sub>. In an <sup>57</sup>Fe Mössbauer spectroscopy study,<sup>3</sup> the spectral shape was found to become asymmetric at a pressure of 4–5 GPa, suggesting a possible shift to AFM order. Magnetization and neutron diffraction measurements up to 0.8 GPa showed a decrease of the static FM moment and an increase of the AFM fluctuation intensity.<sup>4</sup> A parallel can also be made between high pressure and doping with Co, where AFM order appears in Ce(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub> for  $x=0.07$  with  $T_N$  of the order of 60 K. With increasing cobalt concentration,  $T_N$  reaches a maximum of about 90 K for  $x=0.15$ , then decreases for higher concentrations.<sup>5</sup> A high pressure resonant x-ray magnetic scattering study<sup>6</sup> showed that for the  $x=0.07$  crystals, the Néel temperature  $T_N$  increases with pressure, whereas for  $x=0.1$ ,  $T_N$  decreases. This would replicate the effect of cobalt doping although a discrepancy exists between this latter re-

sult and high pressure magnetization measurements<sup>7</sup> where  $T_N$  was found to increase for samples with  $x=0.1$ . Magnetization measurements are one of the few macroscopic techniques (available under pressure) able to distinguish unambiguously between AFM and FM order. However, static magnetization measurements are usually limited to pressures below about 1 GPa, which is too low to usefully study pure CeFe<sub>2</sub>. Therefore, we applied a recently developed very high sensitivity ac susceptibility technique<sup>8</sup> to extend this kind of measurement on pure and cobalt doped CeFe<sub>2</sub> to higher pressures.

### II. EXPERIMENTAL DETAILS

For this study, new batches of pure and cobalt doped single crystals of CeFe<sub>2</sub> were grown using the self-flux technique<sup>9</sup> with cobalt concentrations of  $x=0$ ,  $x=0.07$ , and  $x=0.2$ . The samples were characterized by transport and specific heat measurements to determine the ordering temperatures. The Curie temperature  $T_C$  for the pure CeFe<sub>2</sub> crystals was found to be 229 K, and  $T_C$  for the cobalt doped system with  $x=0.07$  ( $x=0.2$ ) was 198 K (179 K). The Néel temperature for the doped  $x=0.07$  samples ( $x=0.2$ ) was 67.5 K (88 K). All these temperatures are compatible with the nominal cobalt concentrations to within about 1%. The resistivity of the pure CeFe<sub>2</sub> crystals was measured down to 0.05 K. The low temperature behavior follows a  $T^2$  law, with a coefficient of about  $0.04 \mu\Omega \text{ cm}/\text{K}^2$  and a residual resistivity of about  $0.5 \mu\Omega \text{ cm}$ , attesting to the excellent quality of the samples. This is in agreement with a previous report,<sup>10</sup> but the residual resistance ratio in these new samples is about 160, which is almost five times better than any other reported result. The ac susceptibility was measured in a moissanite anvil cell using the technique described in Ref. 8, where a pickup coil consisting of about ten turns of 12  $\mu\text{m}$  diameter copper wire is inserted in the sample chamber. The primary coil placed outside the sample chamber produced an excitation field of about 1 Oe at a frequency of 733 Hz. For most of the experiments, the pressure transmitting medium was Daphne oil. This medium provides good hydrostatic conditions up to about 3 GPa, and quasihydrostatic conditions at

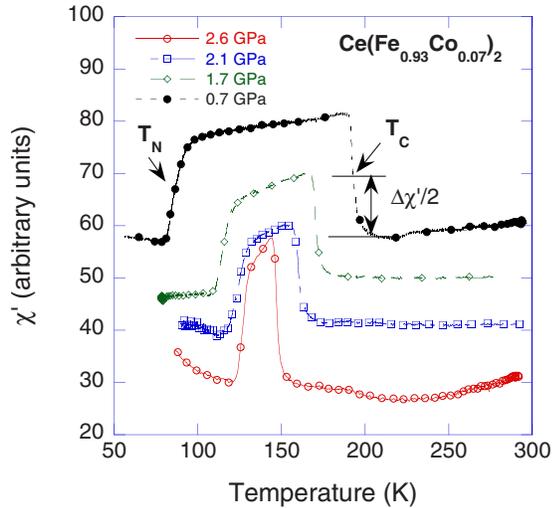


FIG. 1. (Color online) ac susceptibility curves for a single crystal of  $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$  with  $x=0.07$  at different pressures. On cooling, the sharp increase of  $\chi'$  corresponds to the onset of ferromagnetic order, and the decrease at lower temperature corresponds to the ferromagnetic to antiferromagnetic order transition. The transition temperatures are determined as the temperature where half the total jump has occurred.

higher pressures. The pressure was measured using the standard ruby fluorescence technique at room temperature. The pressure change on cooling is estimated to be less than 0.2 GPa. To check the influence of the transmitting medium in the case of pure  $\text{CeFe}_2$ , a final run was performed with the cell loaded with argon, thus providing excellent hydrostatic conditions. In this case, the pressure was determined by the ruby fluorescence *in situ* at low temperature with an accuracy better than 0.1 GPa. The cell was cooled in a simple cryostat with nitrogen or helium depending on the temperature range.

### III. RESULTS AND DISCUSSION

In Fig. 1, the real part of the susceptibility is shown at different pressures for the  $x=0.07$  cobalt doped system. The curves qualitatively resemble similar measurements at ambient pressure.<sup>11</sup> With increasing pressure, we observe a continuous decrease of  $T_C$  and an increase of  $T_N$ , until at pressures above about 2.6 GPa, we no longer observe any reliable transition. This is probably the indication that a pure AFM phase has been reached, or at least that the FM contribution is too weak to be detected. The results on the  $x=0.2$  compound are similar, except that the relevant pressures are lower. The two obtained phase diagrams are shown in Fig. 2. The implications of this phase diagram will be discussed further on. We now turn to the pure  $\text{CeFe}_2$  system. In Fig. 3, we show the real part of the susceptibility for three pressures. Because of the experimental method, it was not usually possible to obtain a continuous curve over the whole temperature range as the switch between nitrogen and helium perturbed the measurement. However, between the cooling and warming procedures, the whole temperature range was systematically explored. At low pressures, below 1.6 GPa, the

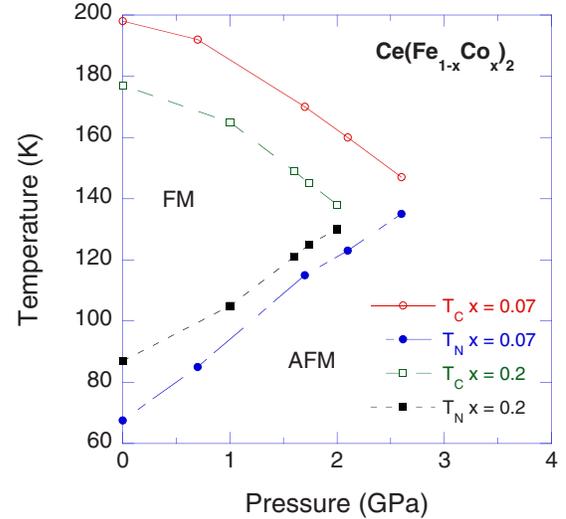


FIG. 2. (Color online) Phase diagram of  $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$  under pressure for  $x=0.07$  and  $x=0.2$ . At higher pressures, no reliable transition was found within the experimental precision.

FM transition appears clearly at the expected temperature [Fig. 3(b)] and no further transition is observed at low temperature. However, at pressures above 2 GPa, a second transition was found, similar to the FM to AFM transition seen in the cobalt doped compound, and almost certainly corresponding to the onset of AFM order in the pure system. With increasing pressure, the behavior is also similar to that found in the cobalt doped compounds: the Curie temperature decreases and the Néel temperature increases until shortly before the two temperatures coincide, and no further reliable signs of a transition are seen. This occurs between 5 and 6 GPa. The results for the phase diagram are shown in Fig. 4,

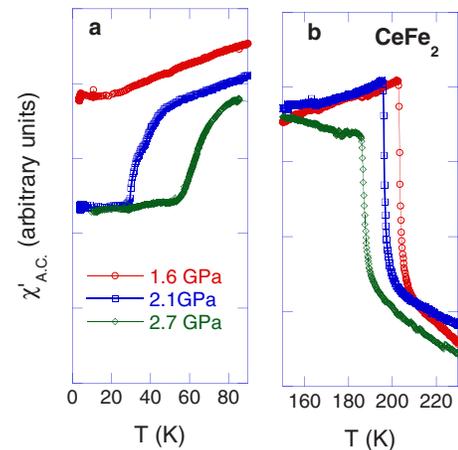


FIG. 3. (Color online) ac susceptibility curves for a single crystal of pure  $\text{CeFe}_2$  at various pressures in the (a) low temperature and (b) high temperature ranges. At pressures below 1.6 GPa, no transition was found at low temperature. However, for  $P>2$  GPa, a relatively sharp decrease in  $\chi'$  was found at low temperature, similar to the transition found in the cobalt doped system and probably corresponding to a transition from ferromagnetic to antiferromagnetic order.

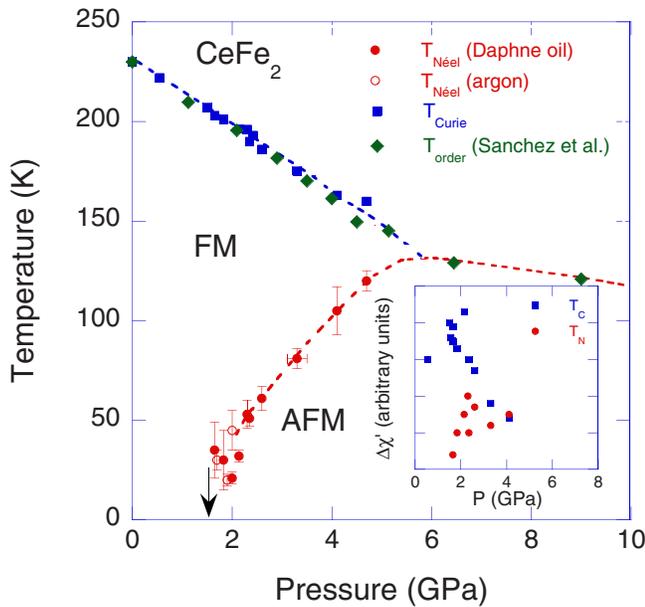


FIG. 4. (Color online) Phase diagram for pure  $\text{CeFe}_2$  under pressure. The arrow marks the highest pressure where no AFM transition was found. The dashed lines are guides for the eye, showing the probable existence of a tricritical point. Green diamonds show the ordering temperature found by Mössbauer spectroscopy (Ref. 3). Solid (open) red circles show measurements using Daphne oil (argon) as pressure medium. The horizontal error bar on the point at about 3 GPa shows the maximum error in pressure determination due to changes on cooling. The error and gradient of pressure for the points measured in argon are less than the size of the points. The scatter of points around 2 GPa and very broad transitions suggest a first order transition at this point. The inset shows the pressure dependence of the size of the jump in  $\chi'$  at the FM and AFM transitions.

where the dashed line shows the results obtained from Mössbauer spectroscopy.<sup>3</sup> The agreement between the two experiments is excellent and several aspects of the Mössbauer study are now clearer. The change in slope in the pressure dependence of the ordering temperature around 5 GPa corresponds to the change to an AFM ground state, thus confirming the authors' speculation that the change in the spectral shape was due to this. The reason that this change was found in the pressure range 4–5 GPa whereas we find the onset of AFM order below 2 GPa is that the low temperature Mössbauer measurements were carried out at 77 K. From our phase diagram, a Néel temperature of 77 K corresponds to a pressure of about 4 GPa.

The most interesting point in the phase diagram of pure  $\text{CeFe}_2$  is potentially the point where AFM order appears at low temperature. If this is a second order transition, it provides the opportunity to study a quantum transition between FM and AFM order, and the various possible phenomena at such a critical point. To study this point in detail, we performed numerous measurements with four different cells to look for the appearance of AFM order in the region 1.6–2 GPa. The lowest pressure where the AFM transition was seen was 1.65 GPa; however, the transitions found at the lowest pressures were invariably broad, with widths of

20–30 K. To reduce pressure gradients, the last cell was loaded with argon, and an *in situ* pressure tuning device<sup>12</sup> was used to finely scan this region. The lowest temperature where the transition was found was about 20 K. The width of the transition cannot be directly related to pressure gradients as broad transitions are also found in the argon loaded cell. Furthermore, the scatter of the points in this region is greater than would be expected from the uncertainties in the pressure determination. This, together with the absence of any clear transition below 20 K, tends to suggest that the switch between a FM and an AFM ground state is a first order transition as indeed is the case for the cobalt doped system. The probable cause for the scatter of points is the sample history (increasing or decreasing pressure and temperature) and the hysteresis of the associated lattice distortion. Of course, the strong decrease in the ac susceptibility is not proof of an AFM ordered phase. However, a return to a paramagnetic phase can probably be ruled out because the Mössbauer results continue to show magnetic order within this phase. There remains the possibility of a state with a FM component. The amplitude of a FM transition measured by ac susceptibility is not a good probe of the moment; however, if we plot the amplitude of the jump at the two transitions (see inset of Fig. 4), we see that the amplitude of the lower transition is initially considerably less than the higher one, but with increasing pressure, the two amplitudes are approximately equal. This suggests that if there is any remaining FM component at high pressure, it is not large. No conclusions can be drawn from the different amplitudes at lower pressure, which could indicate a remaining FM component, an inhomogeneity in the sample with coexisting FM and AFM domains, or just a reduction of the ferromagnetic signal in the ac susceptibility at lower temperatures due to a flatter hysteresis cycle.

The high pressure part of the phase diagram of pure and cobalt doped  $\text{CeFe}_2$  is also of interest. The instability of the FM state arises through the competition between the ferromagnetic Fe  $3d$ -Fe $3d$  interaction, and the antiferromagnetic interaction due to the Ce  $4f$ -Fe  $3d$  hybridization. To explain the phase diagram of the cobalt doped system, where  $T_N$  goes through a maximum and then decreases with increasing cobalt concentration, Fernandez *et al.*<sup>11</sup> proposed that this latter behavior was caused by a weakening of the Ce moment due to the increasing hybridization. Simply drawing a parallel between doping with cobalt and applying pressure, both of which lead to a decrease of the lattice parameters, we might expect the Néel temperature to show a similar behavior, i.e., to increase to a maximum and then decrease. Instead, the effect of pressure is to favor AF order to the extent that the FM state is replaced. This can probably be understood by increasing hybridization due to the reduction of the Ce-Fe distances, but this means that the behavior of the cobalt doped system cannot be understood simply through a volume effect, especially as the volume of the system with the highest  $T_N$  ( $x=0.15$ ) would correspond to a pressure of about only 0.5 GPa (Ref. 13) on pure  $\text{CeFe}_2$  (the bulk modulus<sup>14</sup> is  $B_0=97$  GPa). The phase diagram that is obtained is actually similar to that found by doping not with cobalt but with aluminum,<sup>11</sup> although this might appear surprising as the effect of doping with aluminum is actually to increase the lat-

tice parameter. One important difference between doping with cobalt and aluminum is that, in the first case, the entropy jump at the transition is large, coming not exclusively from the electronic origin but partly from a lattice contribution due to a structural transformation at the transition.<sup>11</sup> It would be interesting to see whether this structural transition is also present in pure CeFe<sub>2</sub> when it becomes antiferromagnetic. The sequence of magnetic structures found here with increasing temperature (AFM-FM-paramagnetic) is quite rare, though not unknown. The cases of Ce<sub>3</sub>Al<sub>11</sub> (Ref. 15) and probably CeAgSb<sub>2</sub> (Ref. 16) are other examples, though in both cases pressures greater than 3 GPa are needed to reach the critical point of the AFM phase compared to less than 2 GPa here, making CeFe<sub>2</sub> a particularly attractive system for future studies. The fact that the FM/AFM instability can be reached by pressure in pure CeFe<sub>2</sub> rather than by doping should also make theoretical approaches easier. Although band structure calculations for CeFe<sub>2</sub> exist,<sup>17</sup> to our knowledge, the question of a volume induced instability to an AFM state has not been examined, and this would be of great interest. Finally, for the cobalt doped system, an important question remains open. Whereas this study and a previous magnetization study<sup>7</sup> find that  $T_N$  increases monotonously with pressure for all values of cobalt doping, the resonant magnetic x-ray (RMXR) experiment<sup>6</sup> seems to show unambiguously that  $T_N$  decreases with high pressure for 10% cobalt doping. Of course, the macroscopic magne-

tization and neutron diffraction experiments are sensitive mainly to the magnetism from the Fe site, whereas RMXR is sensitive only to the moment on the Ce site. If it is confirmed, such different behavior of the ordering temperature on the two sites would be a spectacular though surprising result.

#### IV. SUMMARY

We have prepared very clean single crystals of CeFe<sub>2</sub> and Ce(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>. The magnetic phase diagrams under pressure determined by ac susceptibility show that pressure systematically favors the low temperature AFM state. In the pure CeFe<sub>2</sub> system, the transition to the AFM state at low temperature occurs at less than 2 GPa. This quite low pressure opens up the way for many other types of measurements, including thermodynamic, structural, and neutron scattering studies in order to study in a pure system this low temperature phase which has attracted so much attention in the doped materials.

#### ACKNOWLEDGMENTS

This work was supported by EGIDE under the Alliance program, and the COST scientific program ECOM. We thank J.-P. Sanchez, L. Paolasini, J. Flouquet, and G. G. Lonzarich for valuable discussions.

- 
- <sup>1</sup>O. Eriksson, L. Nordstrom, M. S. S. Brooks, and B. Johansson, *J. Phys. Colloq.* **49**, 693 (1988).  
<sup>2</sup>L. Paolasini, B. Ouladdiaf, N. Bernhoeft, J.-P. Sanchez, P. Vulliet, G. H. Lander, and P. Canfield, *Phys. Rev. Lett.* **90**, 057201 (2003).  
<sup>3</sup>J. P. Sanchez, P. Vulliet, and M. M. Abd Elmeguid, *Hyperfine Interact.* **133**, 5 (2001).  
<sup>4</sup>T. Fujiwara, H. Fujii, Y. Ishii, S. Koiwai, M. Kosaka, Y. Uwatoko, M. Nishi, and K. Kakurai, *Physica B* **312-313**, 336 (2002).  
<sup>5</sup>X. Zhang and A. Naushad, *J. Alloys Compd.* **207-208**, 300 (1994).  
<sup>6</sup>D. Braithwaite, L. Paolasini, P. P. Deen, N. Kernavanois, F. Yakhou, P. Canfield, and G. Lapertot, *Physica B* **378-380**, 782 (2006).  
<sup>7</sup>K. Koyama, K. Fukushima, M. Yamada, T. Goto, Y. Makihara, H. Fujii, and K. Watanabe, *Physica B* **346-347**, 187 (2004).  
<sup>8</sup>P. L. Alireza and S. R. Julian, *Rev. Sci. Instrum.* **74**, 4728 (2003).  
<sup>9</sup>P. C. Canfield and Z. Fisk, *Philos. Mag. B* **65**, 1117 (1992).  
<sup>10</sup>E. Gratz, E. Bauer, H. Nowotny, A. T. Burkov, and M. V. Vedernikov, *Solid State Commun.* **69**, 1007 (1989).  
<sup>11</sup>G. E. Fernandez, M. Gomez Berisso, O. Trovarelli, and J. G. Sereni, *J. Alloys Compd.* **261**, 26 (1997).  
<sup>12</sup>B. Salce, J. Thomasson, A. Demuer, J. J. Blanchard, J. M. Martinod, L. Devoille, and A. Guillaume, *Rev. Sci. Instrum.* **71**, 2461 (2000).  
<sup>13</sup>H. Fukuda, H. Fujii, H. Kamura, Y. Hasegawa, T. Ekino, N. Kikugawa, T. Suzuki, and T. Fujita, *Phys. Rev. B* **63**, 054405 (2001).  
<sup>14</sup>T. Le Bihan and J. P. Sanchez (unpublished).  
<sup>15</sup>J. X. Boucherle, F. Givord, G. Lapertot, A. Munoz, and J. Schweizer, *J. Magn. Magn. Mater.* **144**, 1229 (1995).  
<sup>16</sup>V. A. Sidorov, E. D. Bauer, N. A. Frederick, J. R. Jeffries, S. Nakatsuji, N. O. Moreno, J. D. Thompson, M. B. Maple, and Z. Fisk, *Phys. Rev. B* **67**, 224419 (2003).  
<sup>17</sup>J. Trygg, J. M. Wills, B. Johansson, and O. Eriksson, *Phys. Rev. B* **50**, 4200 (1994).