

Stabilization of antiferromagnetism in CeFe₂ alloys: the effects of chemical and hydrostatic pressure

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Abstract

Effects of Al, Mn and Sb dopings in CeFe₂ and the effect of applied pressure have been investigated. Al doping gives rise to the FM–AFM transition and a reduction in the magnetic moment and T_C values, clearly indicating the growth of the AFM component. Mn and Sb dopings only cause a reduction in the T_C value. It is found that, in general, external pressure enhances the antiferromagnetism in both the pure and the doped alloys. Enhancement of the Ce 4f–Fe 3d hybridization as a result of doping and with the external pressure may be the reason for the stabilization of antiferromagnetism in these alloys.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetism of pure and doped CeFe₂ has attracted considerable interest from researchers for many decades [1–3]. The strong hybridization between Ce 4f and Fe 3d electronic states makes CeFe₂ very special among the series of RFe₂ (R = rare earth) compounds. Although Ce is a light rare earth, 4f electrons hybridize antiferromagnetically with the 3d electrons. This is due to the quenching of the orbital 4f moment by band formation [1]. The lattice parameter, Curie temperature and the magnetic moment show a strong deviation from the normal trend observed in the RFe₂ series [1, 4]. As shown previously, the ground state of CeFe₂ at ambient pressure can be viewed as a canted ferromagnet (FM), i.e. a small antiferromagnetic (AFM) component ($<0.1 \mu_B$) superimposed on a dominant ferromagnetic component [5].

It was predicted that, with the application of pressure, the magnetic moments of Fe and Ce would decrease rapidly. Theoretical calculations have shown that, with a compression of the unit cell by about 6–7%, the compound loses most of its magnetic properties, thereby becoming paramagnetic [6].

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It was experimentally found that at 220 kbar and at low temperatures CeFe₂ loses its magnetism [7]. Nevertheless, it is clear that this critical pressure is considerably lower than that estimated for YFe₂ (1050 kbar [8]). Further comparison with YFe₂ shows that, at low pressures, the Curie temperature increases with pressure for YFe₂ [9], whereas it decreases in CeFe₂ despite a continuous decrease of the iron moment in both compounds. This again indicates that CeFe₂ occupies a special position amongst the RFe₂ compounds [7].

Enhancement of antiferromagnetic spin correlations has been shown in CeFe₂ single crystals at pressures up to 8 kbar [10]. A recent pressure study on CeFe₂ single crystals shows that the transition to the AFM state at low temperatures occurs at pressures less than 20 kbar [11]. They have also found that the temperature at which it undergoes the antiferromagnetic transition (at the Néel temperature, T_N) increases monotonically with pressure. Neutron diffraction studies indicate that the static Fe magnetic moment is suppressed to be only half of that under $P = 1$ bar at 5 K and that the antiferromagnetic spin fluctuation with a propagation vector $q = (1/2, 1/2, 1/2)$ is enhanced by applying a hydrostatic pressure of 15 kbar [12].

On the other hand, it is also well known that, at ambient pressure too, the stabilization of the antiferromagnetic component in CeFe_2 can be achieved with the help of the substitution of small amounts (3–6%) of selected elements such as Co, Al, Ga, Ru, Ir, Os and Re [2, 3, 13]. The first-order nature of the FM–AFM transition (on cooling) gives rise to distinct features of super-cooling/super-heating and kinetic arrest behavior [14]. It is worth noting that, among these substitutions, while Al causes an increase in the lattice parameter, Co results in lattice contraction. However, surprisingly in both these cases, the AFM spin correlations get enhanced, giving rise to the stable low temperature AFM state. Therefore, it is clear that the chemical pressure (positive or negative) alone is not responsible for the stabilization of the AFM state. The effect of external pressure has been reported on a few substituted CeFe_2 compounds as well [15, 16].

The moments on the trivalent Ce ion and Fe in the CeFe_2 series are $2.54 \mu_B$ and $1.77 \mu_B$, respectively [17]. From the polarized neutron study of CeFe_2 , Ce and Fe moments are found to be $-0.14 \mu_B/\text{atom}$ and $1.17 \mu_B/\text{atom}$, respectively [18]. Due to hybridization of Ce 4f and Fe 3d electronic states, Ce remains in the mixed valance state (+3.29) rather than its normal trivalent state in CeFe_2 and this must be the reason for the anomalous magnetic moments of Ce as well as Fe in CeFe_2 . Therefore, it is of interest to investigate the effect of pressure created by chemical substitution (chemical pressure) and by external means (hydrostatic pressure) on the magnetic properties. With the view of comparing the pressure effects in different doped CeFe_2 compounds which undergo lattice expansion and contraction as a result of substitutions, we report pressure studies on Al-, Mn- and Sb-doped CeFe_2 . The compounds studied in this work are CeFe_2 , $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ ($x = 0.01, 0.025$ and 0.05), $\text{Ce}(\text{Fe}_{0.95}\text{Mn}_{0.05})_2$ and $\text{Ce}(\text{Fe}_{0.95}\text{Sb}_{0.05})_2$. While Al and Mn doping are known to cause lattice expansion, Sb causes lattice contraction.

2. Experimental details

Polycrystalline CeFe_2 , $\text{Ce}(\text{Fe}_{0.95}\text{Mn}_{0.05})_2$, $\text{Ce}(\text{Fe}_{0.95}\text{Sb}_{0.05})_2$ and $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ ($x = 0.01, 0.025$ and 0.05) compounds have been prepared by arc-melting the stoichiometric proportion of the constituent elements of at least 99.9% purity in a water-cooled copper hearth in an argon atmosphere. The resulting ingots were turned upside down and remelted several times to ensure homogeneity. The as-cast samples were annealed for ten days in the sequence: 600°C for two days, 700°C for five days, 800°C for two days and 850°C for one day [2]. The structural characterization of these annealed compounds was done by room temperature powder x-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation. XRD data was refined by the Rietveld refinement method using the *Fullprof* suite of programs. Structural parameters have been calculated from this refinement. Magnetization measurements have been performed in a vibrating sample magnetometer attached to a Physical Property Measurement System (PPMS, Quantum Design Model 6500) and/or a SQUID magnetometer. The magnetization measurements under applied pressures have

been carried out using a Cu–Be clamp-type cell attached to the SQUID magnetometer. The maximum pressure that can be obtained in the cell was 10 kbar. Magnetization has been measured in zero-field-cooled (ZFC), field-cooled cooling (FCC) and field-cooled warming (FCW) modes. The sample was in the form of a small piece weighing a few tens of milligrams and of irregular shape.

3. Results and discussions

$\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ ($x = 0, 0.01, 0.025$ and 0.05)

Room temperature x-ray diffraction patterns along with the Rietveld refinement plots confirm the phase purity of all the compounds. All of them possess the cubic structure with space group: $Fd\bar{3}m$. The lattice parameters are found to increase as Al concentration increases from 0 to 0.05.

Figure 1(a) shows the temperature variation of magnetization data at a low field of $H = 500$ Oe for pure and Al-doped samples at ambient pressure. While the parent compound, CeFe_2 , shows a normal ferromagnetic behavior with a Curie temperature (T_C) of 230 K [19], Al-doped compounds show the stabilized AFM state at low temperatures, in agreement with earlier reports [2, 20]. There is a significant reduction in T_C with substitution of Al along with an increase in the FM–AFM transition temperature, T_N . Both these observations point towards the fact that the AFM strength increases with Al. In figure 1(b), magnetization data is shown for $x = 0.01$ in different fields. The effect of an external field is to reduce the AFM coupling and favor an FM behavior in the material. With the increase in field, the T_C values increase and the T_N values decrease. The difference between ZFC and FCW data increases with the increase in field, which is consistent with our recent results on Ga-substituted CeFe_2 [19]. It is clear from figure 1(b) that the AFM phase is very strong at 0.5 kOe, but the strength decreases as the field is increased to higher values. This gives rise to the bifurcation between the ZFC and the FCW data at 20 and 50 kOe.

Figures 2(a)–(c) shows the temperature dependence of magnetization at different pressures for $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ compounds with $x = 0.01, 0.025$ and 0.05 . In all three compounds, with the increase in pressure the T_C decreases and the T_N increases, which suggests that the effect of external pressure is to stabilize the AFM phase. The magnetization values also decrease with pressure. These observations are due to the pressure-induced enhancement of antiferromagnetic correlations in the system. With pressure the widening of the Ce f level occurs which in turn enhances hybridization between Ce 4f and Fe 3d electronic states. As a result, the Fe–Fe exchange interaction responsible for the Curie temperature gets weaker and the outcome is a decrease of T_C and an increase of T_N . Another important observation from figure 2 is that the difference between ZFC and FCC data increases with the increase in pressure. This can be understood in the following way. The FM–AFM transition in these compounds is known to be accompanied by a structural transition (at T_N) from cubic to rhombohedral structure [2]. Because of this magnetostructural coupling, the increase of pressure

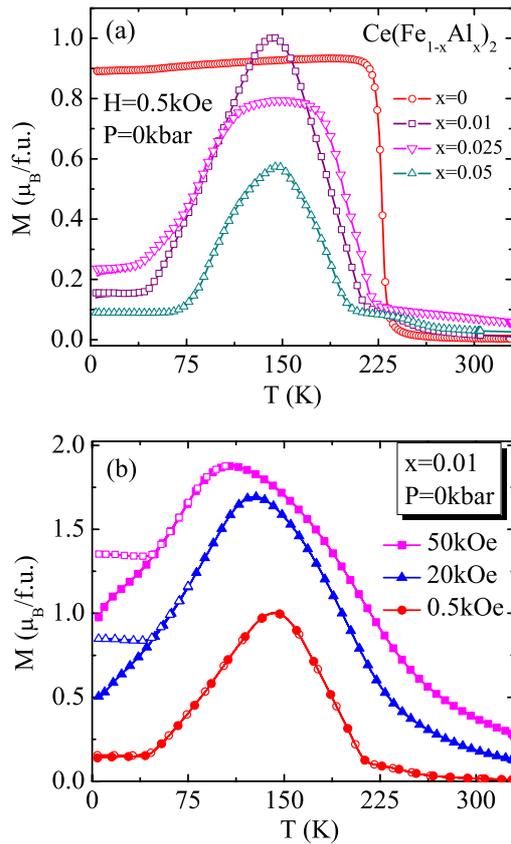


Figure 1. (a) Temperature dependence of the magnetization of $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ compounds for $x = 0, 0.01, 0.025$ and 0.05 . (b) Temperature dependence of ZFC and FCW magnetization of $\text{Ce}(\text{Fe}_{0.99}\text{Al}_{0.01})_2$ in different applied fields. Open and closed symbols refer to FCW and ZFC modes of data, respectively.

prefers the rhombohedral phase. Therefore, the magnetization variation during cooling (FCC) and heating (ZFC) is expected to be different. This is because the energy barrier that the system encounters during heating and cooling will be different. This explains the considerable ZFC–FCC difference at higher pressures, compared to that at ambient pressure.

Figure 3(a) shows the five-loop $M(H)$ isotherm at $T = 2.8$ K under ambient pressure ($P = 0$ kbar) for the $x = 0.01$ compound. This measurement has been made with a field sweep rate of 100 Oe s^{-1} . The sample was zero-field-cooled from room temperature (paramagnetic region) to the measurement temperature. With increasing field, the moment shows a rapid initial increase, then becomes flat and shows a smooth jump at a critical field $H_C \sim 28$ kOe. The moment does not get saturated even in a field of 70 kOe. Between increasing and decreasing cycles, a large hysteresis is observed, but with zero coercivity. This observation confirms the first-order nature of the magnetic-field-induced AFM to FM transition. Another observation to be noticed here is that the virgin curve remains outside the envelope curve, which was also observed earlier for $x = 0.04$ [20]. Super-cooling and kinetic arrest associated with the first-order transition are responsible for this behavior [20]. With an increase in the concentration of Al, the antiferromagnetic correlation increases, as reflected by the increase in the critical field values

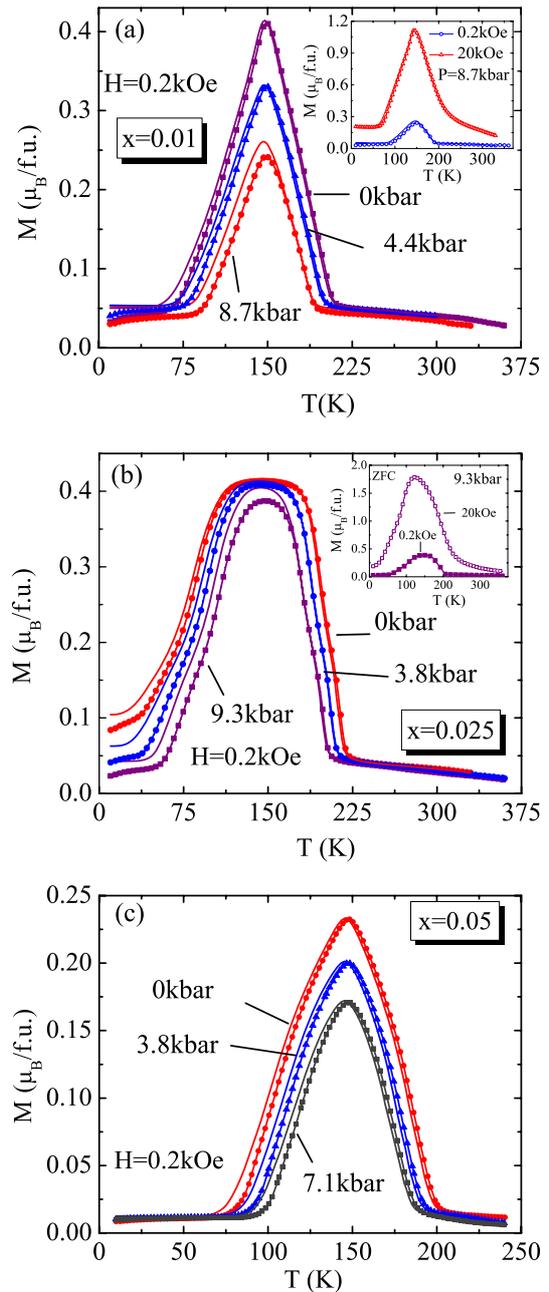


Figure 2. Temperature variation of magnetization in ZFC and FCC modes under various applied pressures for the compounds (a) $x = 0.01$, (b) $x = 0.025$ and (c) $x = 0.05$. In each plot filled symbols refer to ZFC and solid lines refer to FCC data. The insets in (a) and (b) are the M – T curves at two different fields at the highest pressure.

shown in figure 3(b). Although Al substitution causes an increase in the lattice parameter, it shows an effect similar to that with applied hydrostatic pressure. It may be due to modification in the density of states (DOS) around the Fermi level with Al substitution. Another point to be noted is that at 8 K the fifth loop follows the same path as the first loop, which is not the case at $T = 2.8$ K (see figure 3(a)). This indicates that thermal fluctuations reduce the effects associated with the kinetic arrest of the FM phase.

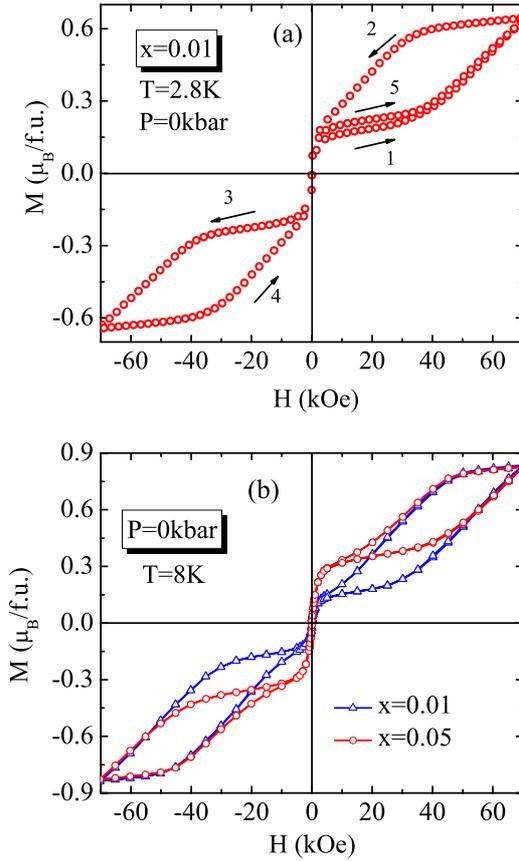


Figure 3. (a) $M-H$ isotherms at $T = 2.8$ K at ambient pressure for $\text{Ce}(\text{Fe}_{0.99}\text{Al}_{0.01})_2$. Arrows indicate the direction of field in which data have been taken. (b) $M-H$ loops at $T = 8$ K for $x = 0.01$ and 0.05 .

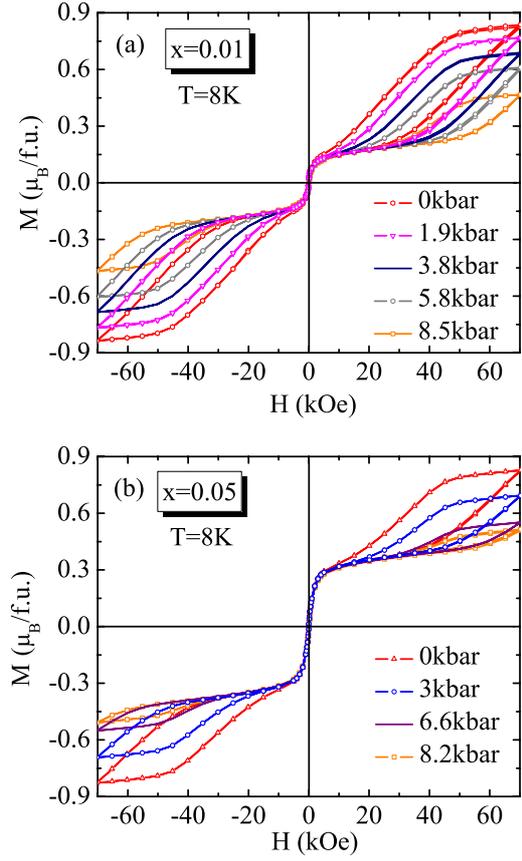


Figure 4. M versus H loop at $T = 8$ K under various pressures for (a) $x = 0.01$ and (b) $x = 0.05$ compounds.

In figures 4(a) and (b), the nine-loop magnetization isotherms are shown for $x = 0.01$ and 0.05 at 8 K and at various pressures. For this measurement also, the sample was zero-field-cooled from the paramagnetic region to 8 K and then the data was taken in increasing and decreasing modes for both positive and negative fields. For a given pressure, there is no difference between the data in the first and second cycles of magnetic field variation. The $M-H$ behavior is almost identical to that seen in figure 3(b). Here also, the moment does not get saturated at a field of 70 kOe. With pressure the critical field (H_C) increases and the moment reduces considerably. The effect of pressure seems to reinforce the $3d-4f$ hybridization present in Al-doped CeFe_2 compounds which in turn reinforces the AFM correlations in the material. This gives rise to an increase in H_C as shown in figure 5. Comparison of 8 and 50 K data in figure 5 implies that thermal fluctuation converts the system towards a more parallel alignment of moments, reducing the H_C values. The decrease in moment seen in figure 4 can also be attributed to the enhanced hybridization with pressure.

It can be noticed that the AFM-FM transition in Al-doped compounds is rather smooth, unlike the case in Ru-, Re- and Ga-doped compounds [19, 21]. Furthermore, the region of existence of ferromagnetism is very narrow (see figures 1 and 2) in the Al-doped case as compared to other substitutions. Similarly, the $M-H$ isotherms at temperatures below T_N in

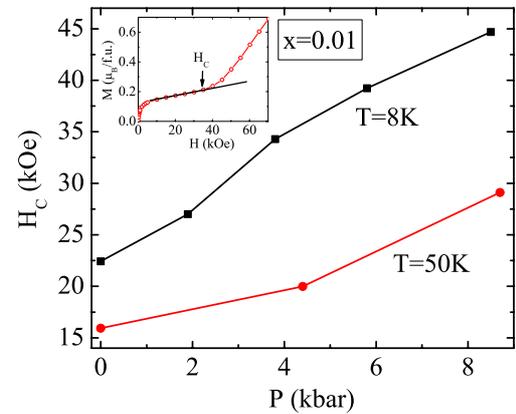


Figure 5. Pressure dependence of critical field in $\text{Ce}(\text{Fe}_{0.99}\text{Al}_{0.01})_2$ at different temperatures.

the case of Ru-, Re- and Ga-doped compounds are generally accompanied by multiple sharp jumps. Such jumps are absent in the case of Al-doped compounds. Kennedy *et al* have shown that there is a broad overlap between two magnetic phases (AFM and FM) in the case of Al doping compared to the narrow overlap seen with other dopants [3], which may be the reason for the smooth transition in the former. The application of magnetic field at low temperatures favors the FM phase and, as the field is increased, the volume ratio of the FM phase to

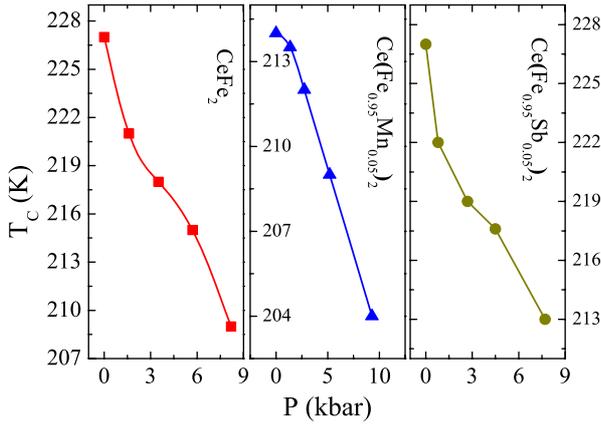


Figure 6. Variation of Curie temperature (T_C) with external pressures for undoped, Mn- and Sb-doped CeFe₂ compounds.

the AFM phase evolves gradually in this case, due to a broad overlap region between these phases. So, instead of getting sharp jumps in the magnetization isotherms, a smooth behavior is found across the field-induced AFM–FM transition.

Mn- and Sb-doped CeFe₂ compounds

At ambient pressure, Mn-doped CeFe₂ compounds are known to be ferromagnets [22, 23]. Likewise, we find that Sb substitution also does not stabilize the AFM fluctuations. Even a pressure of about 9 kbar is not able to stabilize the AFM phase at low temperatures in both these compounds. However, there is a monotonic reduction in the ferro–para transition temperature, (T_C) in both cases, as shown in figure 6, which also shows the variation in pure CeFe₂. As observed in the earlier section, pressure has a considerable effect on the hybridization between the Ce 4f and Fe 3d electronic states. It is clear from figure 6 that the pressure dependence of T_C is maximum in CeFe₂, whereas it is lower in both Mn- and Sb-doped compounds. In fact, the pressure dependence seen in these two cases is found to be nearly equal to that of Al-doped compounds. Therefore, it is clear that the effect of applied pressure is maximum in CeFe₂, as there is no chemical pressure in the undoped case. Like in Al-doped compounds, the pressure seems to enhance the 3d–4f hybridization in Mn- and Sb-substituted compounds to such an extent that there is a reduction in T_C . However, this hybridization is not enough to result in a strong AFM state as seen in the Al doping.

At ambient pressure, the saturation moments are 2.6 and 2.7 μ_B /f.u. for CeFe₂ and Ce(Fe_{0.95}Mn_{0.05})₂, respectively, at 8 K. With the application of pressure no significant change is observed in these values. On the other hand, at ambient pressure, in Ce(Fe_{0.95}Sb_{0.05})₂, the moment is 3.3 μ_B /f.u. which reduces to 2.6 μ_B /f.u. at the highest pressure. Another interesting observation in the case of Ce(Fe_{0.95}Sb_{0.05})₂ is the metamagnetic transition found at $P = 2.7$ kbar (see the inset of figure 7). At higher pressures, a similar transition seems to appear at fields above 75 kOe. The presence of a metamagnetic transition indicates that the system possesses an AFM state, at least in very small fraction, at low temperatures, though the M versus T curve does not show any clear evidence of this fact.

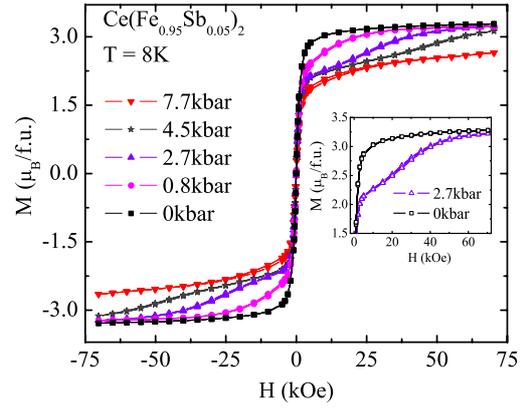


Figure 7. Isothermal magnetization loops at $T = 8$ K for Ce(Fe_{0.05}Sb_{0.05})₂. The inset shows the first quadrant of the M – H loop at ambient pressure and at 2.7 kbar.

However, this tendency is in agreement with the reduction in T_C seen in figure 6.

Therefore, it is clear that there is an enhancement in the AFM component in the case of Mn and Sb doping in CeFe₂, though a transition to the AFM state is not observed. This may be due to the fact that the 4f–3d overlap increases only nominally in the case of Mn and Sb doping or these substitutions may be unable to change the DOS near the Fermi level in such a way as to stabilize the AFM state in these materials.

4. Conclusions

We have shown the pressure effect on the magnetization of the undoped and doped CeFe₂ compounds. It is found that, in general, external hydrostatic pressure enhances the AFM component in doped CeFe₂. The increase in the T_N values and the decrease in the magnetic moment and T_C values clearly show the growth of the AFM component. The results have been discussed on the basis of the mixed valent behavior of Ce ion as well as the change in the hybridization between the Ce 4f and Fe 3d electronic states. External pressure seems to enhance the hybridization present in these materials. Results obtained on different dopings indicate that it is not the ionic radii, but the extent of hybridization and modification in the mixed valency that are responsible for the stabilization of the antiferromagnetic phase. Detailed band structure calculations on all these dopings and experimental data using techniques like photoelectron spectroscopy are essential to unravel the underlying physics of the anomalies observed in different dopings. The effect of external pressure observed here opens up the opportunity to theoretically model these materials.

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