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Magnetic properties of $Ce_2Fe_{17}H_x$ hydrides under hydrostatic pressure

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Abstract

The $Ce_2Fe_{17}H_x$ ternary hydrides with $x = 0.8$ and 2 have been studied under external pressures up to 1.2 GPa in order to check the stability of H-induced ferromagnetism. The resulting T vs. P phase diagrams allow valuable comparisons with the x vs. T ones if hydrogen (x) is assumed to act as a negative pressure tool. © 1997 Elsevier Science S.A.

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1. Introduction

The $Ce_2Fe_{17}H_x$ series of metal hydrides was recently and systematically studied for its structural and magnetic characteristics [1–4]. Most of the R_2Fe_{17} binary alloys exhibit ferromagnetic characteristics, except some of the compounds with a small R element (i.e. Ce, Yb, Lu). At low temperatures in these compounds, some local antiferromagnetic Fe–Fe interactions stabilise a long period oscillating structure. The absorption of hydrogen, e.g. in the Ce_2Fe_{17} alloy, increases the interatomic distances and consequently the Fe–Fe distance, so that ferromagnetic correlations are favoured again [1]. In a recent article, the magnetic characteristics of the $R_2Fe_{17}H_x$ series of hydrides have been analysed in terms of the localised vs. moving picture of the 3d magnetic moment; the magnetoelastic parameters being activated by a so-called negative pressure via hydrogen insertion in the interstitial sites [3]. In order to confirm the magnetic characteristics of these systems and the related reverse transformations, the application of an external pressure on hydrides appears fully relevant. Owing to the approximate scale factor, i.e. 1 hydrogen atom is approximately −0.8 GPa [4], here we have gathered results obtained mainly on the lightly H-charged hydrides ($x = 0.8$, 2), with reference to the upper pressure limit of the experimental set-up (approx. 1.5 GPa).

2. Experimental

The polycrystalline samples were synthesised starting from high purity elements (3 N grade) melted in the cold crucible of a high frequency furnace. After verification of the phase quality by X-ray diffraction, which showed a unique Ce_2Fe_{17} rhombohedral phase, weighted amounts of crushed and sieved powder (40 μm grain size) were introduced in a dedicated stainless steel autoclave. High purity (5 N grade) hydrogen gas was admitted at selected pressures to reach the

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final stoichiometry. Next, a gravimetric method was used to control the exact hydrogen composition.

In this article, systematic magnetic studies under pressure with $Ce_2Fe_{17}H_x$ compounds with $x=0.8$ and 2 are presented. The a.c. susceptibility measurements under 10 Oe of excitation field were carried out in the fully hydrostatic pressure mode up to 1.2 GPa, in the temperature range of 80–400 K. An GCA-10 compressor was used with helium gas as the pressure transmitting medium. A manganin pick-up coil placed in the chamber was used to calibrate the pressure.

3. Results and discussion

The a.c. susceptibility curves recorded between 80 and 300 K for $x=0.8$ in the pressure range 0.01–0.7 GPa are plotted in Fig. 1. Two anomalies are pointed out, the first one T_1 is a kink that takes place at the highest temperature, the second one T_2 is related to the zero pressure behaviour. It corresponds to an inflexion point taking place at a lower temperature, and is more difficult to detect. The T vs. P phase diagram shows a decrease of both these temperature T_1 and T_2 when the pressure is increased Fig. 2.

The first temperature concerns the phase transition between the long period AF state and the paramagnetic one. The relative variation of the ordering temperature with pressure is $dT_1/dP = -25$ K/GPa. The second temperature, T_2, corresponds to the phase transition between the ferromagnetic phase and the long period AF state [5]. Under low pressure and in the 180–230 K temperature range, the long period AF state is stabilised. However, under higher pressures (e.g. greater than 0.9 GPa), the AF state is observed down to 80 K and the ferromagnetic phase is rapidly shifted to the lowest temperatures, then fully superseded. When an external pressure is applied, a new magnetic state takes place at a pressure greater than 0.7 GPa. This pressure-induced state corresponds to the incommensurate long period antiferromagnetic ordering as it was previously observed for the pure Ce_2Fe_{17} and parent alloys [5–7].

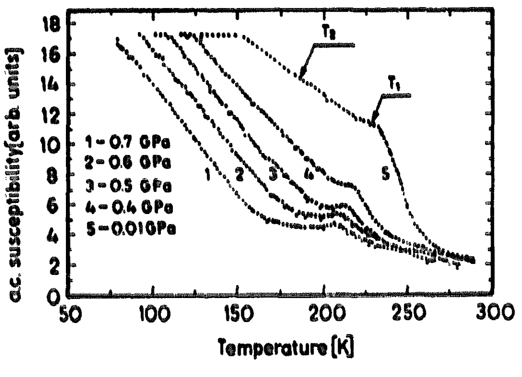

Fig. 1. a.c. susceptibility runs vs. temperature for $Ce_2Fe_{17}H_{0.8}$ at different pressure values.

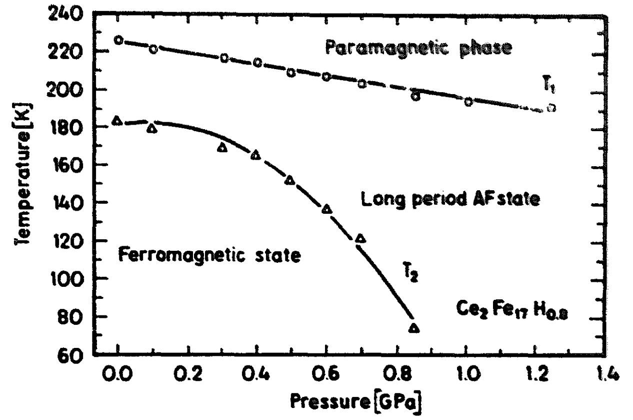

Fig. 2. A pressure vs. temperature magnetic phase diagram for $Ce_2Fe_{17}H_{0.8}$.

Figure 3 plots the a.c. susceptibility records of $Ce_2Fe_{17}H_2$ measured vs. the temperature and under external pressure. For the richer hydrogen compound which is spontaneously ferromagnetic, no shoulder corresponding to an AF long period to a paramagnetic state was observed above T_1. Only the inflexion point corresponding to T_2 is pointed out. For the pressure range of 0.01–1.2 GPa, the $x=2$ compound exhibits ferromagnetic properties only. However, under a pressure of 1.25 GPa the a.c. susceptibility curve shows evidence of slight changes of shape. It could be suggested that a new AF state is induced as was found in the case of $Ce_2Fe_{17}H_{0.8}$, when an external pressure greater than 1.4–1.5 GPa was applied. The relative variation of the ordering of temperature with pressure is $dT_1/dP = -62$ K/GPa. It corresponds to a much faster rate in comparison with the previous compound ($x=0.8$). However, the normalised variation of the ordering of temperature vs. pressure to the hydrogen content is exactly the same for both compounds, i.e. -31 K/GPa per H atom. This is fully consistent with what was already measured on different members of the series of ternary hydrides $Ce_2Fe_{17}H_x$ with $x=0$, 0.8, 1, 2 and 3 (Fig. 4). The greater the increase of the ordering temperature (mostly Curie temperature that is found proportional to the absorbed hydrogen amount), the untidier the decrease (dT_2/dP) due to the external pressure application. When expanding the lattice upon hydrogen insertion, the negative pressure effect has been estimated from T_C increases measured on different ternary hydrides with Y, Th and all the rare earth series, to about -40 K per H atom [8]. In the present experiment one must account for the presence of the additional interstitial atoms in the cell even if they are small, but making the lattice much more rigid. Moreover, changes in the d band

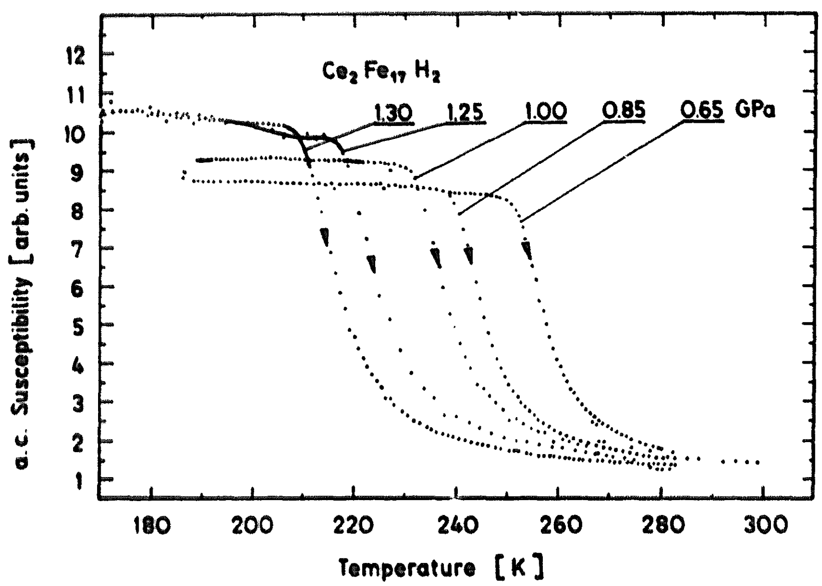

Fig. 3. a.c. susceptibility runs for $Ce_2Fe_{17}H_2$ at different pressure values. At a pressure of 1.25 GPa, a kink is observed on the susceptibility curve around 210 K.

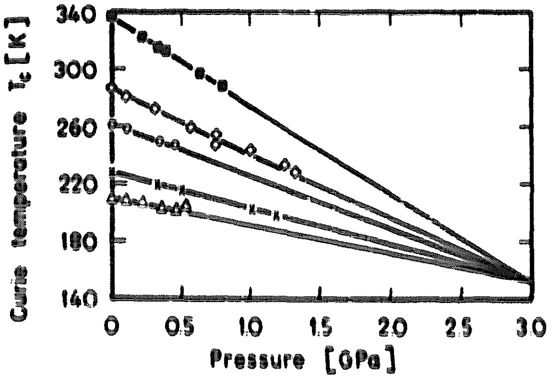

Fig. 4. A temperature vs. pressure magnetic phase diagram for several contents of hydrogen in the $Ce_2Fe_{17}H_x$ system. All the variations of the ordering temperature can be linearly extrapolated to a singular point (150 K × 30 GPa).

filling should result from some s–d electron transfers upon hydrogen insertion.

It is noteworthy that in Fig. 4 all the plots corresponding to different hydrogen contents can be extrapolated to a single point, that is 150 K × 3 GPa. We estimate that this singular point should correspond to the disappearance of any magnetic ordering in the series, i.e. as the result of competing positive and more and more negative exchange interactions and simultaneously a progressive depolarisation of the d band. Please note that when manganese is substituted to iron the magnetic ordering turns to antiferromagnetism and the corresponding ordering temperature rapidly decreases [9].

X-ray measurements of the lattice parameters were carried out between $T = 100$ K and $T = 300$ K. All spectra have been indexed within the frame of R-3m space group. A comparison with the cell dimensions of the starting alloy shows that the thermal expansions in the hydride are comparable to what was observed for the a and c parameters in systematic analysis [8]. In reference to this work, it could be proposed that the decrease in the Fe–Fe dumbbell distance under pressure should be considered the pertinent one for the change from positive to negative exchange d–d couplings. With the moderately charged $Ce_2Fe_{17}H_x$ hydrides ($x = 0.8, 2$), this is in relation to the range of weak and intermediate pressures only, i.e. when magnetic ordering turns from ferromagnetism to the long-range antiferromagnetic type of ordering.

4. Conclusion

We conclude that in the $Ce_2Fe_{17}H_x$ series with $0 < x < 4.8$, the compensation of an internal chemical pressure created by hydrogen atom insertion may be almost achieved for an external pressure of approximately 1–2.5 GPa depending on the hydrogen content. In light of the present results, a systematic neutron diffraction analysis would be highly desirable to fully characterise the magnetic structure under pressure. Not only must this be performed on differently charged hydrides and at intermediate pressure ranges in order to elucidate the AF long period — ferromagnetic transformation, but also in the limit pressure range of about 3 GPa where magnetism should be unstable. These experiments are now scheduled in forthcoming investigations at JINR Dubna (Russia). With reference to a previous analysis [3,4], magnetism in the $R_2Fe_{17}H_x$ ternary hydrides should be considered as mostly of the localised type, this character being reinforced upon hydrogen insertion. Under limited external pressure this should apply again, but at the limit of 3 GPa the moving picture of magnetism should apply even better.

Acknowledgements

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