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Magnetic relaxation phenomena in R_2Fe_{17} (R=Y, Dy, Er, Ho) and C and H derivatives

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Abstract

The ac susceptibility anomalies present in the R_2Fe_{17} (R=Y, Dy, Er and Ho) and in the C and H interstitial compounds were studied. They are caused by disaccommodation of vacancies and hopping of H atoms coupled to the domain walls. The activation energies of the relaxation processes were determined.

Keywords: Permanent magnets; Gas solid reaction; X-ray diffraction; Magnetic measurements

Recently we have studied the ac susceptibility relaxation anomalies in the $R_2Fe_{14}B$ compounds and found that they are caused by magnetic disaccommodation and interstitial hopping [1]. The R_2Fe_{17} compounds may also be subject to the same type of relaxation processes. For example, the light rare earth substituted Sm_2Fe_{17}, which has no SRT in the whole thermal range, shows a clear anomaly around 165 K [2]. The insertion of N, C [3], H or D [4] has been reported to induce anomalies due to reversible and irreversible relaxation.

In the present paper we report on the anomalies present in the pure R_2Fe_{17} (R=Y, Dy, Ho and Er compounds, and their hydrogenated and carbonated interstitial derivatives.

The stoichiometric compounds were synthesized by arc melting. To obtain the carbides, carbon grains were interspersed among the stoichiometric compounds and then remelted. The maximum amount of C charging was evaluated as $x=1.2\pm0.1$. The hydrogen uptake was performed in an autoclave at 370 K temperature and $P=5$ MPa pressure. The charge was $x=3.5\pm0.2$. In both cases x was determined from weight analysis and X-ray diffraction (XRD) determination of the lattice constants expansion (Table 1). The stoichiometric R compounds have the hexagonal Th_2Ni_{17} structure $P6_3/mmc$, different to the light R compounds which crystallize in the rhombohedral (R-3m). The charged compounds we have prepared remain in their majority phase hexagonal, except the Y compounds which clearly consist of both phases; the hexagonal content being 87% for the pure, 40% for the carbide and 30% for the hydrogenated compound, as determined from XRD. It is reported that for $x\geqslant1$ in the carbides a rhombohedral phase should become the majority [5,7]. Since our XRD results indicate the persistence of the hexagonal phase in the $R_2Fe_{17}C_{1.2\pm0.1}$, we suggest that it may have become favored due to the preparation process.

The octahedral sites 6h at mid-edges of the Fe_6R

Table 1
Cell parameters and average activation energies for pure and charged R_2Fe_{17}

Compound	a (Å)	c (Å)	E_{a1} (eV) at T_1	E_{a2} (eV) at T_2
Dy_2Fe_{17}	8.464(0)	8.302(1)		0.65±0.02
$Dy_2Fe_{17}C_{1.2}$	8.548(1)	8.366(1)		0.58±0.02
$Dy_2Fe_{17}H_{3.5}$	8.564(0)	8.343(0)	0.34±0.02	0.66±0.02
Ho_2Fe_{17}	8.444(1)	8.286(1)		0.53±0.05
$Ho_2Fe_{17}C_{1.2}$	8.542(1)	8.352(1)		0.58±0.07
$Dy_2Fe_{17}H_{3.5}$	8.553(0)	8.329(0)	0.34±0.04	0.58±0.02
Er_2Fe_{17}	8.432(1)	8.285(1)		0.64±0.05
$Er_2Fe_{17}C_{1.2}$	8.536(0)	8.360(1)		0.58±0.07
$Er_2Fe_{17}H_{3.5}$	8.510(0)	8.312(0)	0.27±0.03	0.58±0.05
Y_2Fe_{17} Hex	8.475(1)	8.292(1)		–
Rho	8.507(3)	12.360(7)		
$Y_2Fe_{17}C_{1.2}$ Hex	8.594(2)	8.331(2)		0.44±0.07
Rho	8.602(2)	12.494(4)		
$Y_2Fe_{17}H_{3.5}$ Hex	8.589(2)	8.342(2)	0.34±0.04	0.67±0.67
Rho	8.638(3)	12.506(7)	0.22±0.05	

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hexagons are occupied by both C and H atoms, up to a maximum of 3 atoms p.f.u., while the tetrahedral sites (12*i*) within the Fe_6 hexagons may also be occupied by a maximum of one or two H atoms [6]. From the magnetic point of view, charging with C and H is known to maintain unchanged the basal anisotropy of these compounds, except for $Er_2Fe_{17}C$ which undergoes a spin reorientation transition at about 100 K [7].

The two components, χ' and χ'', of the susceptibility, χ_{ac} (T), were measured in a mutual inductance ac susceptometer, from 77 K to room temperature (RT) with an excitation field of $h_0 = 1$ Oe and 12 Hz$<\nu<$1.2 kHz. The measurements were performed on oriented powders fixed with epoxy, with the easy magnetization direction (EMD) parallel to the ac exciting field.

To illustrate our results we only show data of the Dy compounds (Fig. 1). The phenomenology observed is similar irrespective of the R partner. The $\chi'_{ac}(T)$ curve at fixed frequency always shows two peaks, one at $T_1 \approx 140$ K and at $T_2 \approx 240$ K (Fig. 1, left). The value of T_1, for pure and carbide compounds, is not frequency dependent (insets Fig. 1, right); it has the characteristic behavior of the anomalies due to magnetic disaccommodation [1]. In contrast, the anomaly at T_2 has a strong frequency dependence; it can be explained in terms of a Debye type of relaxation, with an average relaxation time associated to

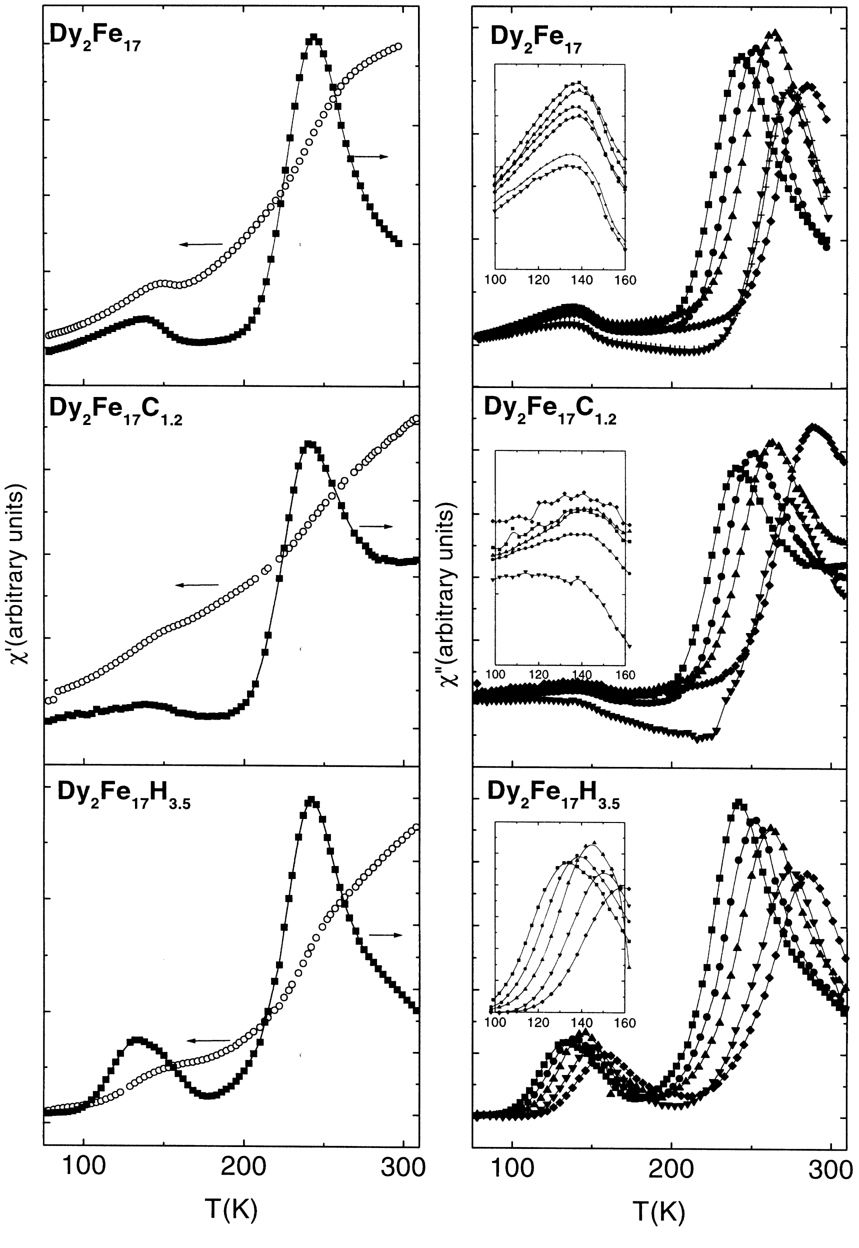

Fig. 1. Left: $\chi'(T)$: open circles, and $\chi''(T)$: solid squares, of Dy_2Fe_{17}, $Dy_2Fe_{17}C_{1.2}$ and $Dy_2Fe_{17}H_{3.5}$, measured at $\nu = 12$ Hz. Right: $\chi''(T)$ at 12 Hz (squares), 36 Hz (circles), 120 Hz (up triangles), 360 Hz (down triangles), 480 Hz (crosses) and 1200 Hz (diamonds). Insets: magnification of the T_1 peaks.

an average activation energy E_{a2} such that $\tau = \tau_0 \exp(E_{a2}/k_B T)$. The maximum in χ'' takes place at the temperature when the condition of $\tau = 1/\omega$, where $\omega = 2\pi\nu$, is fulfilled. The exception is Y_2Fe_{17} for the anomaly at T_2 is mixed up with the ordering transition and E_{a2} cannot be deduced.

The effect of carbon charging on the anomaly temperatures is minimal; the anomalies at T_1 and T_2 remain frequency independent and dependent, respectively. The value of E_{a2} is, within experimental error, almost identical to the pure compound. In this case the $Y_2Fe_{17}C_{1.2}$ compound is not exceptional and has both T_1 and T_2 anomalies.

The effect of H charging modifies substantially the nature of the T_1 anomaly; now both, at T_1 and T_2, are frequency dependent. The Debye process at T_1 has $E_{a1} \approx 0.3$ eV. For $Y_2Fe_{17}H_{3.5}$ the low temperature anomaly segregates into two frequency dependent peaks which drive to two values of the activation energy (Table 1).

The experimental conclusion of this work is that the Debye process at T_2 is common to all compounds, irrespective of the R atom involved and the presence or absence of interstitial atoms. $E_{a2} \approx 0.6$ eV which is indicative of short range processes. This anomaly is caused by the domain wall motion which is excited by the ac field. The walls are coupled to entities like defects, impurities, lattice vacancies, etc. If the coupled nonmagnetic entity becomes mobile by thermal activation, then the domains wall motion reflects that mobility in the relaxation time and corresponding activation energy. Since the domains and domain wall types are most surely similar for all the studied compounds, given their common structure and magnetic ordering, on one hand, and the same preparation method of the as-cast material, on the other, it could be expected to find the same E_{a2} values, as found. Since we observe the same reversible process for all pure and charged compounds it needs to be of intrinsic nature, and thus, probably related to the relaxation of stoichiometric vacancies, as proposed earlier for $Sm_2Fe_{17}H_x$ [4]. The disaccommodation anomalies at T_1 are due to the same relaxation process, however, this maximum takes place at the temperature when $\tau_e \approx \tau$, where the characteristic experimental time τ_e is the point to point measuring time [1].

In addition, the hydrogenated compounds also show a low temperature frequency dependent anomaly. It is known that interstitial H atoms may be quite mobile in compounds like the $R_2Fe_{14}BH_x$ compounds [1]. Thus, in the $R_2Fe_{17}H_{3.5}$ compounds the Debye process with $E_{a1} \approx 0.3$ eV is ascribed to the jumps of the H atoms; the anomaly is due to the coupling of the domain walls to H. We conjecture that the most probable process is that of the $12i$–$12i$ jumps for two reasons: the tetrahedral sites are less stable than the octahedral ones [8], and in a recent Mössbauer study on the related $Pr_2Fe_{17}H_x$ evidence was found that H atoms in the equivalent sites jump between the six available sites in each Fe_6 hexagon [9].

The segregation into two peaks, with two activation energies, of the $Y_2Fe_{17}H_{3.5}$ compound is probably due to the simultaneous presence of the rhombohedral and hexagonal phases. Though the insertion sites are very similar in the two phases, the detailed interatomic distances to the neighbors are different.

Concluding, we have explained the different effects that the H and C insertion has on the ever-present anomalies in the susceptibility due to domain wall motion coupled to vacancies and H interstitials excited by a low frequency ac field, and obtained the average activation energies involved in both types of processes.

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