

MAGNETIC PROPERTIES OF THE PSEUDO-BINARY INTERMETALLIC
COMPOUNDS $(\text{Ce}_x\text{Y}_{1-x})\text{Fe}_2$

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Abstract

Magnetic susceptibility and Mössbauer spectroscopy measurements on cubic Laves phase pseudo-binary compounds $(\text{Ce}_x\text{Y}_{1-x})\text{Fe}_2$ are reported. The thermal variation of the magnetization and the dependence of the hyperfine interactions, Curie temperature, saturation moments at 4K and lattice parameter on concentration are presented. The results show a difference in behaviour between the regions rich in Ce and in Y, which is attributed to a possible change of the valence of Ce.

The direction of easy magnetization at 77K changes from $\langle 111 \rangle$ in YFe_2 to $\langle 101 \rangle$ in the pseudo-binary compounds rich in Ce.

1. Introduction

The intermetallic compounds CeFe_2 and YFe_2 are well known to crystallize as MgCu_2 -type Laves phases. These binary compounds have been studied from the point of view of their magnetic properties and hyperfine (hf) interactions [1-6]. For a general review of the magnetism of intermetallic compounds formed with rare-earth and 3d metals see reference [7]. Measurements of magnetization on the $(\text{Ce}_x\text{Y}_{1-x})\text{Fe}_2$ compounds have been reported [8].

The aim of this work is to study the properties of the $(\text{Ce}_x\text{Y}_{1-x})\text{Fe}_2$ pseudo-binary compounds in order to investigate the possibility of change of the valence of Cerium ion (which is 4^+ in CeFe_2) when CeFe_2 is diluted in a matrix of a RFe_2 compound with a larger lattice parameter and formed with a trivalent rare-earth-like metal (Y).

We have studied the structural parameters, the magnetic properties and hyperfine interactions at Fe sites of $(\text{Ce}_x\text{Y}_{1-x})\text{Fe}_2$ compounds with $x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$.

2. Experimental

The samples were prepared by melting stoichiometric amounts of the components in an arc furnace under an argon atmosphere. The nominal purity of the constituents was: Ce and Y 99,97% (Rare Earth Products Ltd.), Fe 99,99% (Johnson Matthey Inc.). The buttons were melted two or three times, and homogenized for a week at 800-900°C in an argon atmosphere.

The samples were examined by X-ray powder photographs,

using Fe K α radiation and an Mn filter, with an exposure time of 48 hours. They were found to be single-phase; the lattice parameters were derived by least-squares analysis using Nelson-Riley's extrapolation.

Magnetization measurements were made using a P.A.R. vibrating sample magnetometer over a temperature range 4.2 K - 750 K in magnetic fields up to 14.5 kG, with the samples under He gas. The Curie temperatures T_c were determined by extrapolation of the $M_g^2 \times T$ curves obtained at low field (500G).

Mössbauer measurements were made at 77 K in a flow cryostat. The calibration and the linearity of the scale were checked several times; a velocity range sufficiently wide to include the outer peaks of the iron spectrum was used to check for the presence of free iron in the intermetallic compounds. The absorbers were prepared by mixing the powdered samples with small amounts of silicon grease to afford protection against oxidation.

3. Results and Discussion

The pseudo-binary compounds $(Ce_x Y_{1-x})Fe_2$ examined were found to crystallize in the cubic $MgCu_2$ (C15) structure, as already observed for the binary compounds $CeFe_2$ and YFe_2 . The lattice parameters vary about 1% along the series, from 7.298 Å for $CeFe_2$ to 7.359 Å for YFe_2 . The dependence of a_0 with concentration shows a positive deviation from Vegard's law being linear in the range $0.2 \leq x \leq 1$ and levelling off near the YFe_2 end (Fig. 1).

The temperature dependence of the magnetization at constant magnetic field (10 kG) is shown in Fig. 2. All the compounds order magnetically. In the curves of magnetization versus field, no hysteresis was observed.

The Curie temperatures T_c obtained show a roughly linear dependence with concentration, from 532 K for YFe_2 to 237 K for $CeFe_2$ (Fig. 3), with a small deviation for x smaller than 0.4.

The saturation magnetic moments per formula unit, μ_{sat} were derived from measurements of the magnetization at 4.2 K as a function of the applied magnetic field extrapolated to $H \rightarrow \infty$. These moments do not vary linearly with x (Fig. 3). The curve of μ_{sat} versus concentration can be divided into two distinct regions, corresponding roughly to the first half and second half of the concentration range.

The Mössbauer spectra (Fig. 4) were computer analysed as a superposition of lorentzian lines of equal width. The parameters derived from the fits were the magnetic splitting, quadrupole splitting, isomer shifts, widths, and intensities of each doublet in the six-line patterns.

The mean values of the magnetic hf fields H_{hf} and electric quadrupole interactions $E_q = e^2qQ(3\cos^2\theta - 1)/2$ for the series obtained from fits with six lines are given in Fig. 5. The plot of the values of magnetic hf field shows a non-linear variation with Ce concentration. The values of H_{hf} decrease slowly in the first half of the series and, for $x \geq 0.6$, decrease more abruptly. The quadrupole interaction E_q goes through a minimum for $x = 0.4$. The values of isomer

shift are practically constant with concentration.

The direction of easy magnetization in YFe_2 has been found to be $\langle 111 \rangle$ from the shape of the Mössbauer spectrum [6]. In this case the spectrum consists of two superposed sets of six lines, with intensities in the ratio 3:1, corresponding to two sites that, although crystallographically equivalent, are unequivalent when the sample is magnetized. In the compound $CeFe_2$ at low temperatures, the direction of magnetization could not at first be derived with certainty [3], although further studies have suggested a magnetization parallel to $\langle 100 \rangle$ [4], a case in which the spectrum presents only six lines. The latter observation was confirmed by a detailed analysis of Mössbauer data as a function of temperature [5]. These authors found a change in the direction of magnetization above 150 K, the magnetization moving from the $\langle 100 \rangle$ direction to another direction in the (110) plane.

The spectra described in the present work, when analysed in terms of two sets of six lines, gave better computer fits under the hypothesis of intensity ratio 3:1 (i.e. direction $\langle 111 \rangle$) for the compounds rich in Y, and intensities 1:1 (direction $\langle 101 \rangle$) for those rich in Ce (excluding $CeFe_2$). For $CeFe_2$ there are apparently only six lines, but there is a small asymmetry in the line intensities (also noticeable in other published spectra) which remains unexplained.

The linewidths obtained from the computer fits with 12 lines (intensities 3:1 in the first half and 1:1 in the second half) increase towards the middle of the concentration range (see Fig. 5), due to the degree of disorder in the system, which is expected to be maximum near $x = 0.5$. This

arises from the distribution of configurations, seen by the ^{57}Fe probes. The presence of such distribution makes the determination of the direction of easy magnetization (and consequently of the best hypothesis for the fit) more difficult.

To discuss the general trends in the system, we have given in Fig. 5 the magnetic hyperfine fields derived from computer fits with six lines only, and therefore represent average values for the two magnetic sites.

The most significant Mössbauer result obtained in the present work is the difference in slope of the two halves of the graph of \bar{H}_{hf} versus concentration (Fig. 5). This difference is strongly correlated to the difference in the concentration dependence of the magnetic moment in the two regions of concentration (Fig. 3).

A shift in the direction of magnetization can produce a discontinuous variation in the hf field at the Fe sites, due to a difference in the lattice magnetic dipole sums [3]; the present variation in average H_{hf} leads us to think rather in terms of a change in the electronic structure along the series.

The difference in slope in the two halves of the curve of \bar{H}_{hf} (Fig. 5) and the same general behaviour present in the curve of magnetic moment and M_g versus T can be understood in the following way. Starting from CeFe_2 , we have a pseudo-binary compound AFe_2 where A is an alloy of Y^{3+} and Ce^{4+} ; if this process continued, we would naively expect a linear dependence of \bar{H}_{hf} or μ_{sat} with concentration. The observed change

in slope deviates from simple dilution behaviour, probably due to the fact that the Cerium valence changes, tending to 3+ when diluted in the matrix of YFe_2 . Consequently A is an alloy of two trivalent metals, and it is reasonable to expect in such an alloy a smaller rate of change of the band magnetic properties with concentration. The small dip in μ_{sat} at $x = 0.2$, still significant compared to the experimental uncertainties, may be accounted for by the magnetic moment that appears at the cerium atom (Ce^{3+} is magnetic). A similar antiparallel coupling of a light rare-earth moment to μ_{Fe} has been observed in SmFe_2 [8,9]. A dip in μ_{sat} is not visible in the curve of reference [8] since there are no results in the concentration range $x = 0.1 - 0.4$.

The lattice parameter of a compound " $\text{Ce}^{3+}\text{Fe}_2$ " would be of the order of 7.5 \AA , as can be extrapolated from the plots of a_0 versus atomic number for the RFe_2 compounds [2]. Therefore, alloying " $\text{Ce}^{3+}\text{Fe}_2$ " to pure YFe_2 would initially increase a_0 of the pseudo-binary compounds. Our X-ray data do not show an increase, but show a constant a_0 near the YFe_2 limit (Fig. 1).

In conclusion, our results show a markedly different behaviour from the one expected for simple dilution. This suggests the existence of a drastic change in the electronic structure, possibly a change of the valence of the Cerium ions.

Measurements of μ_{sat} as a function of pressure and lattice parameter as a function of temperature are under way to obtain further information on this system.

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FIGURE CAPTIONS

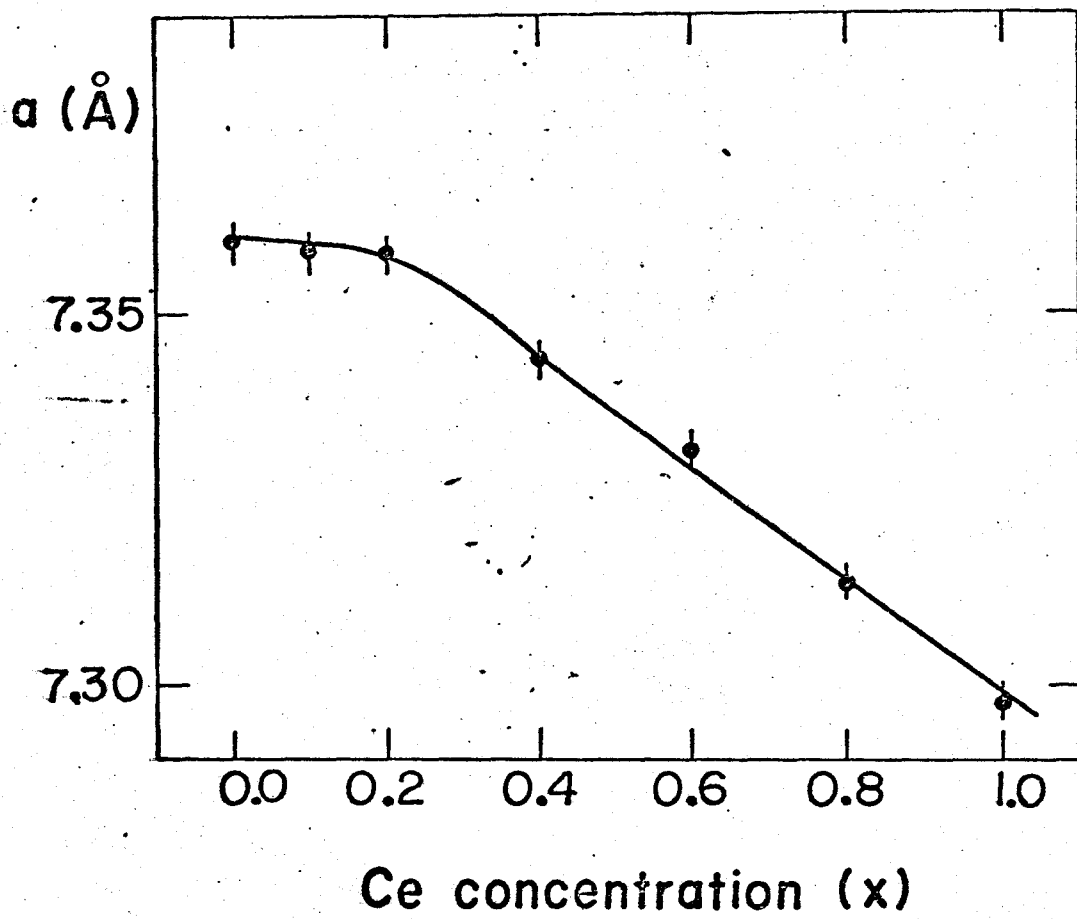
Fig. 1 - Lattice parameter of $(\text{Ce}_x\text{Y}_{1-x})\text{Fe}_2$ as a function of concentration.

Fig. 2 - Isofield (10 KG) thermal variation of the magnetization for $(\text{Ce}_x\text{Y}_{1-x})\text{Fe}_2$.

Fig. 3 - Saturation magnetic moment μ_{sat} at 4.2K and T_c as a function of concentration.

Fig. 4 - Concentration dependence at 77K of: a) Average Magnetic hyperfine field (\bar{H}); b) Electric quadrupole interaction (E_q); c) linewidths (W).

Fig. 5 - Mössbauer spectra at 77K of Fe^{57} in $(\text{Ce}_x\text{Y}_{1-x})\text{Fe}_2$. Numbers in each spectrum are x value.



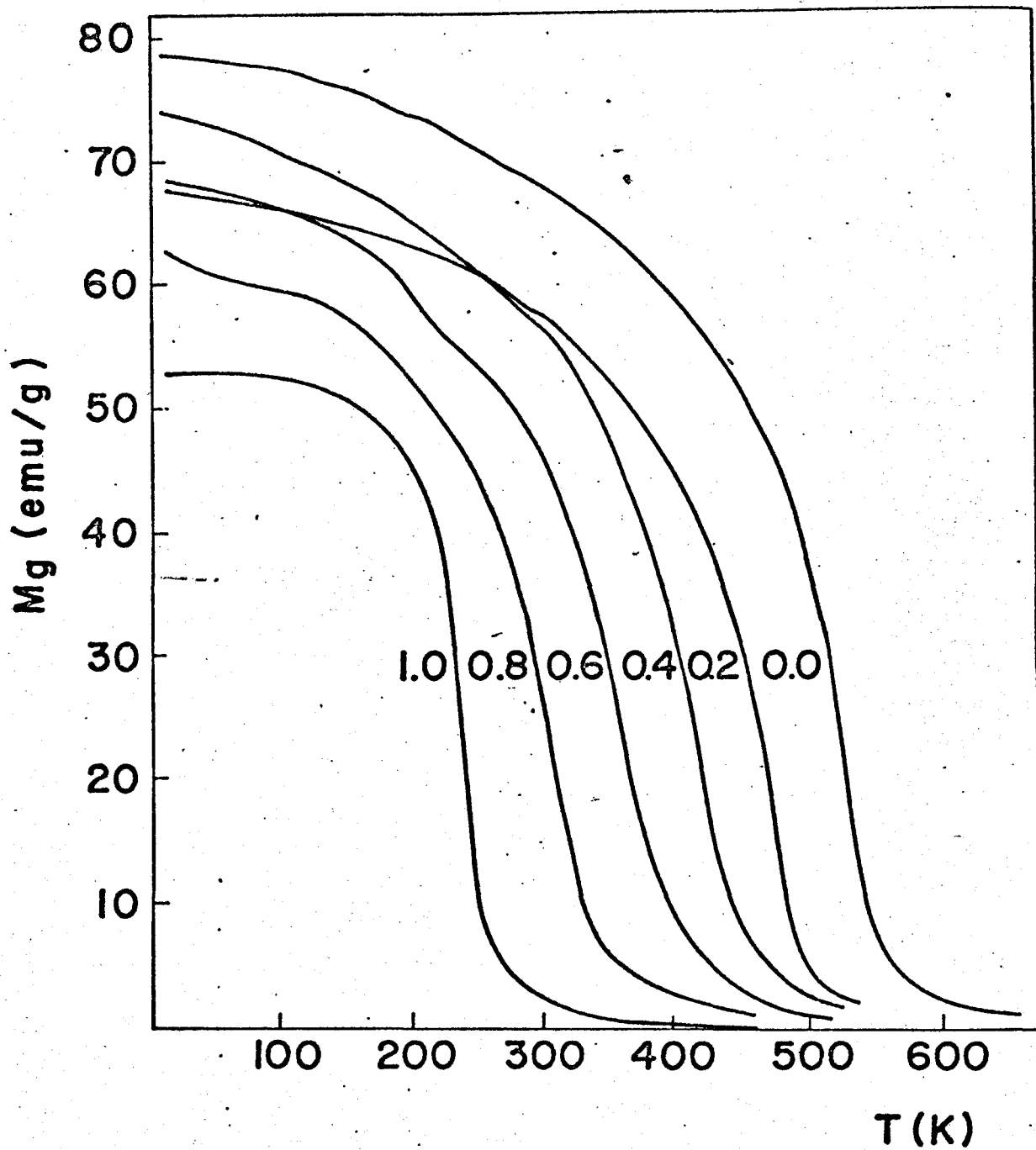


Fig. 2

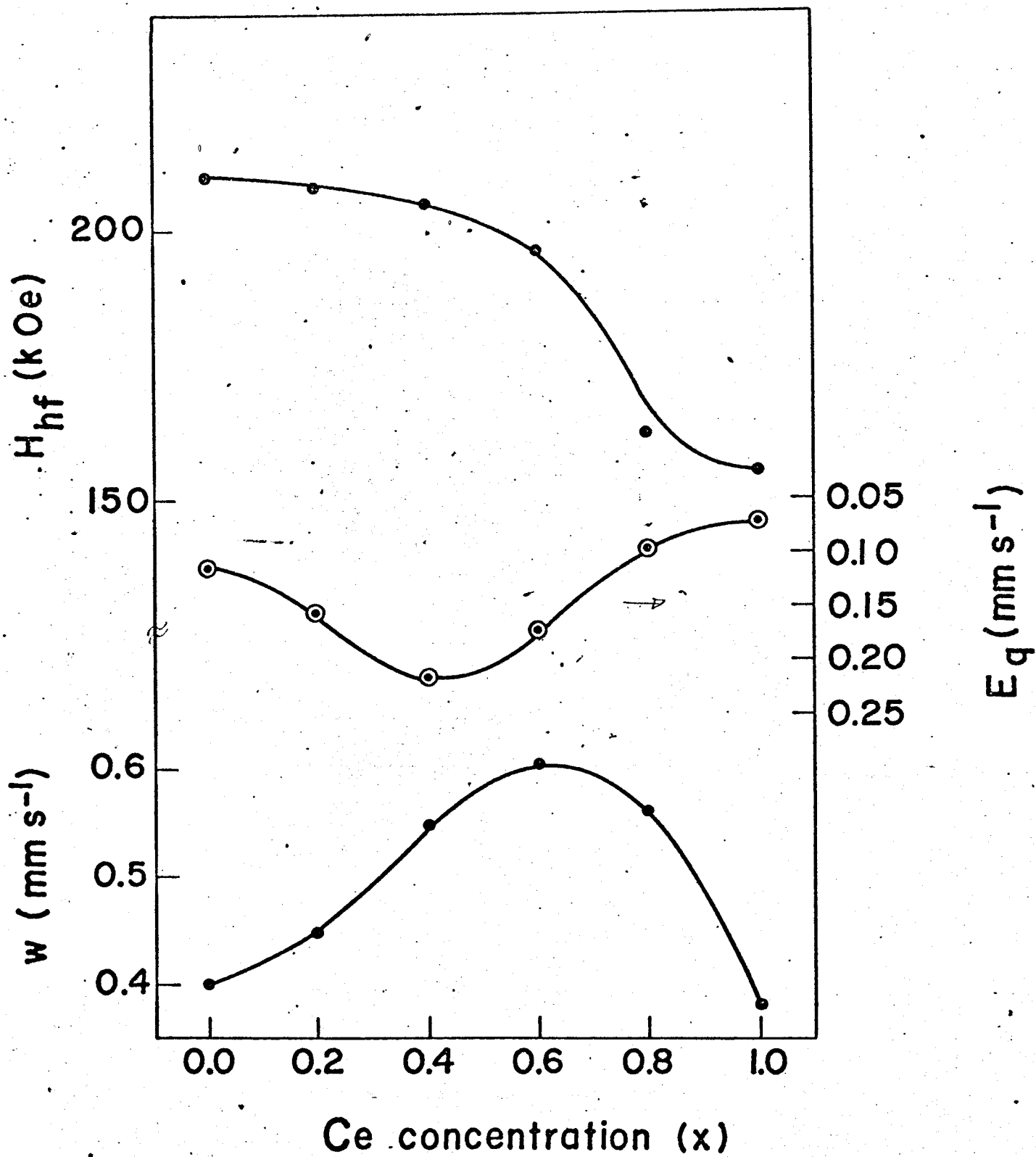


Fig 4

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