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# MOSSBAUER STUDIES OF DILUTE ERBIUM IMPURITIES IN ZIRCONIUM HYDRIDES

by

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# Mössbauer Studies of Dilute Erbium Impurities in Zirconium Hydrides*

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Resumé - On présente les spectres hyperfins d'impuretés d'erbium diluées dans le composés $\delta$-$ZrH_{1.5}$ de structure fluorite et $\varepsilon$-$ZrH_{1.87}$ de structure fluorite avec une distorsion tetragonale. Les spectres hyperfins sont identiques dans les deux cas et revelent un environnement cubique de l'ion Er, indépendament de la structure crystallographique de la matrice; ce fast revele la formation d'un agregat cubique Er-hydrogene. Les frequences de relaxation paramagnetique sont également identiques dans les deux cas, malgré les modifications importantes des densités d'etat électronique. Les mechanismes de formation de tels agrégats Er-hydrogene sont discutés.

Abstract - Hyperfine spectra are reported for Er present as a dilute impurity in the fluorite structure compound $\delta$-$ZrH_{1.5}$ and the tetragonally distorted fluorite $\varepsilon$-$ZrH_{1.87}$. In both cases, the hyperfine spectra are identical and show cubic symmetry around the Er ion regardless of the host crystal structure, showing the formation of a locally cubic Er-hydrogen cluster. Paramagnetic relaxation frequencies are also identical in the two phases, in spite of large changes in the electronic density of states. Mechanisms for the formation of such Er-hydrogen clusters are discussed.

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## INTRODUCTION

Zirconium metal forms two single-phase hydrides, labelled ε and δ, which have vastly different properties (Fig. 1). At hydrogen to metal ratios H/Zr between 1.5 and 1.6, the δ-phase is obtained with the fluorite structure. For H/Zr between 1.7 and 2.0, this distorts into the tetragonal ε-phase [1]. Along with this phase transformation, dramatic changes are observed in the electronic properties of the hydrides [2]. For example, in the ε-phase the electron density of states increases when going from the δ-ε phase boundary up to H/Zr = 1.85, then decreases at higher hydrogen concentrations.

A closely related subject involves the migration of charge between hydrogen and metal ions, i.e. whether the hydrogen loses part of its charge to the metal valence band (the "protonic" model) or accepts some charge from the metal atom to become negatively charged (the "anionic" model). Experimental results in the past have generated controversies between the two appraoches [3] with recent XPS studies supporting the anionic model [4].

We have previously shown [5,6] that Mössbauer effect measurements can be used to investigate the electronic properties of rare-earth hydrides. Those studies have provided information on magnetic properties and crystal field interactions, as well as the charge on the hydrogen ions. In the present work we present such a study of $Er^{3+}$ impurities in δ- and ε- phase zirconium hydrides.

## EXPERIMENTAL METHODS AND RESULTS

A solid solution containing approximately 2000 ppm of Ho metal in Zr metal was produced. This was then hydrided to form cubic δ-$ZrH_{1.5}$ and tetragonal ε-$ZrH_{1.85}$. The lattice parameters of both materials were measured and found to be in excellent agreement with published values [2].

The samples were neutron irradiated to produce $^{166}$Ho activity, which decayed ($T_{1/2}$ = 27 hrs.) to give the 80.6 keV Mössbauer transition in $^{166}$Er. The resonance spectra were measured using conventional techniques in a transmission geometry. The single-line absorber was $ErH_2$ held at 4.2 K while the Zr hydride samples containing the $^{166}$Ho were held at various temperatures between 4.2 and 30 K in the exchange gas column of a helium cryostat.

The spectra of $^{166}$Er in δ-$ZrH_{1.5}$ have already been published [7] along with their analysis. In Fig. 2 we have reproduced that data, and in Fig. 3 we show the spectrum of ε-phase $ZrH_{1.85}$, both measured at 4.2 K. The two patterns are remarkably similar, and are also very similar to that measured in a $YH_2$ host, which has the fluorite structure [5,8]. In all cases, these represent nearly static paramagnetic hyperfine patterns of an almost isotropic crystalline electric field (CEF) level of the $Er^{3+}$ ion. This result is not surprising for the cubic $YH_2$ host. However, for the other compounds the point symmetry for the Er ion is not expected to be cubic since in the δ-phase compound one has substantial defects in the fluorite structute, and in the ε-phase one has a tetragonal distortion.

On increasing the temperature for $ZrH_{1.85}$ up to 30 K, changes in the resonance line shape were observed which were characteristic of paramagnetic relaxation effects. Again, these were very similar to those observed in δ-$ZrH_{1.5}$[7].

## DISCUSSION

As we have previously shown [7], the spectra of $Er^{3+}$ in δ-$ZrH_{1.5}$ are characteristic of a $\Gamma_7$ CEF level which has been slightly distorted from cubic symmetry. A similar result is obtained for Er in ε-$ZrH_{1.87}$. Analysis of the spectra at 4.2 K gave g values of $g_x = 6.8 \pm 0.2$, $g_y = 6.8 \pm 0.2$ and $g_z = 6.9 \pm 0.2$, compared with the isotropic value of 6.8 obtained in the pure $\Gamma_7$ state. The results of the analysis of the temperature dependence of the relaxation spectra (see discussion below) indicate that the first excited state is at least 50 K above the ground state. The g values obtained are thus indicative of the true ground state.

The results obtained in both the δ- and ε-phase zirconium hydirdes indicate that the Er impurity does not reflect the nature of the host, but rather forms an impurity state which is roughly independent of the host. Similarity with the spectra obtained in cubic $YH_2$ indicates that this consists of a well-stabilized cubal coordination of eight hydrogen atoms producing a nearly cubic CEF at the impurity site. This complex is so stable that neither the non-stochiometry of the $\delta$-$ZrH_{1.5}$ host nor the tetragonal distortion ($c/a = 0.908$) and small non-stochiometry of the $\varepsilon$-$ZrH_{1.87}$ host are reflected at the Er site.

Additional evidence that the Er ion forms a complex which is not sensitive to the host properties is given by comparing the temperature dependence of the relaxation rates in the two compounds (See Fig. 4). Below 20 K, the primary relaxation mechanism is through Korringa coupling of the impurity spins and conduction electron spins [7]. In such a case, the relaxation rate is proportional to the temperature and to the quantity $[J_{sf}N(E_F)]^2$, where $J_{sf}$ is the exchange integral between the Er 4f spins and the conduction electrons, and $N(E_F)$ is the conduction electron density of states at the Fermi surface. In Fig. 4 we show the temperature dependence of the relaxation rate for both the hydrides. The identical results imply that $J_{sf}N(E_F)$ is the same for both, even though the value for $N(E_F)$ found in specific heat measurements [2] of $ZrH_{1.85}$ is almost twice that of $ZrH_{1.5}$. It is unlikely that the value of $J_{sf}$ has changed in the two phases in such a way that it just compensates the change in $N(E_F)$.

The observation of cubic symmetry in both these non-cubic compounds along with the identity of the relaxation rates in the two cases show that the nature of the host material in this case cannot be explored by the rare-earth impurity. While the $\Gamma_7$ ground state obtained in all cases implies anionic hydrogen ions ($H^-$) [5], this is only a property of the local Er - $H_8$ cluster and is not necessarily a property of the host zirconium hydrides.

In the following we will indicate possible reasons for the formation and unusual stability of the Er-$H_8$ cluster in the δ- and ε-phases of Zr hydride. Since the δ-phase has the same crystal structure as $ErH_2$, the formation of such a cluster implies a stronger chemical bonding between Er and hydrogen as compared to that between Zr and hydrogen. However, since the Goldschmidt atomic diameter in $ErH_2$ is 7% larger than that of Zr in $ZrH_{1.5}$, the cluster will probably be produced with some distortion of the host atoms in the vicinity of the impurity. This is reflected in the deviation of the CEF ground state from the purely isotropic $\Gamma_7$ level. The observation of a cubic cluster in the tetragonal phase is harder to understand. It is clear that no precipitation of the $ErH_2$ phase has occurred since this would result in a spectrum indicative of much faster relaxation times [5]. One can see from the phase diagram (Fig. 1) that upon cooling from room temperature the ε/(δ+ε) phase boundary may be crossed. This may very well result in a nucleation of a small amount of the δ-phase at the Er impurity, leaving a situation which is locally the same as δ-$ZrH_{1.5}$. However, even if the phase boundary is not crossed, the strong bonding strength between the Er and H ions may still allow the precipitation of an additional phase.

# Figure Captions

1. Phase diagram for Zr-H system in the higher concentration range (after [1]).
2. Mössbauer spectrum for $^{166}$Er as a dilute impurity in δ-ZrH$_{1.5}$ at 4.2 K. The solid curve is a fit including paramagnetic relaxation effects as discussed in the text.
3. Mössbauer spectrum for $^{166}$Er as a dilute impurity in ε-ZrH$_{1.87}$.
4. Temperature dependence of paramagnetic relaxation frequency for Er impurity in δ- and ε-phase of Zr hydrides.

## References

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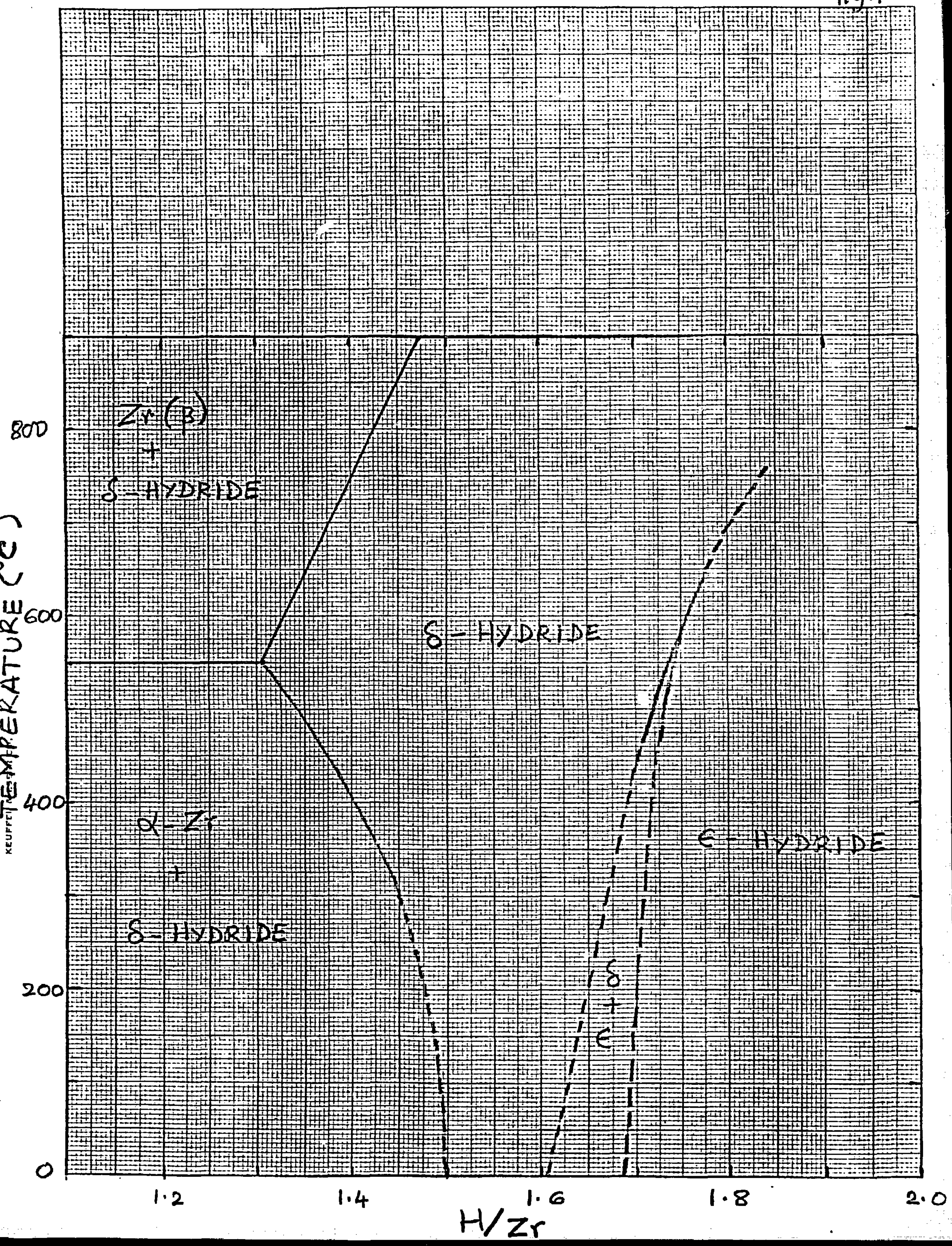
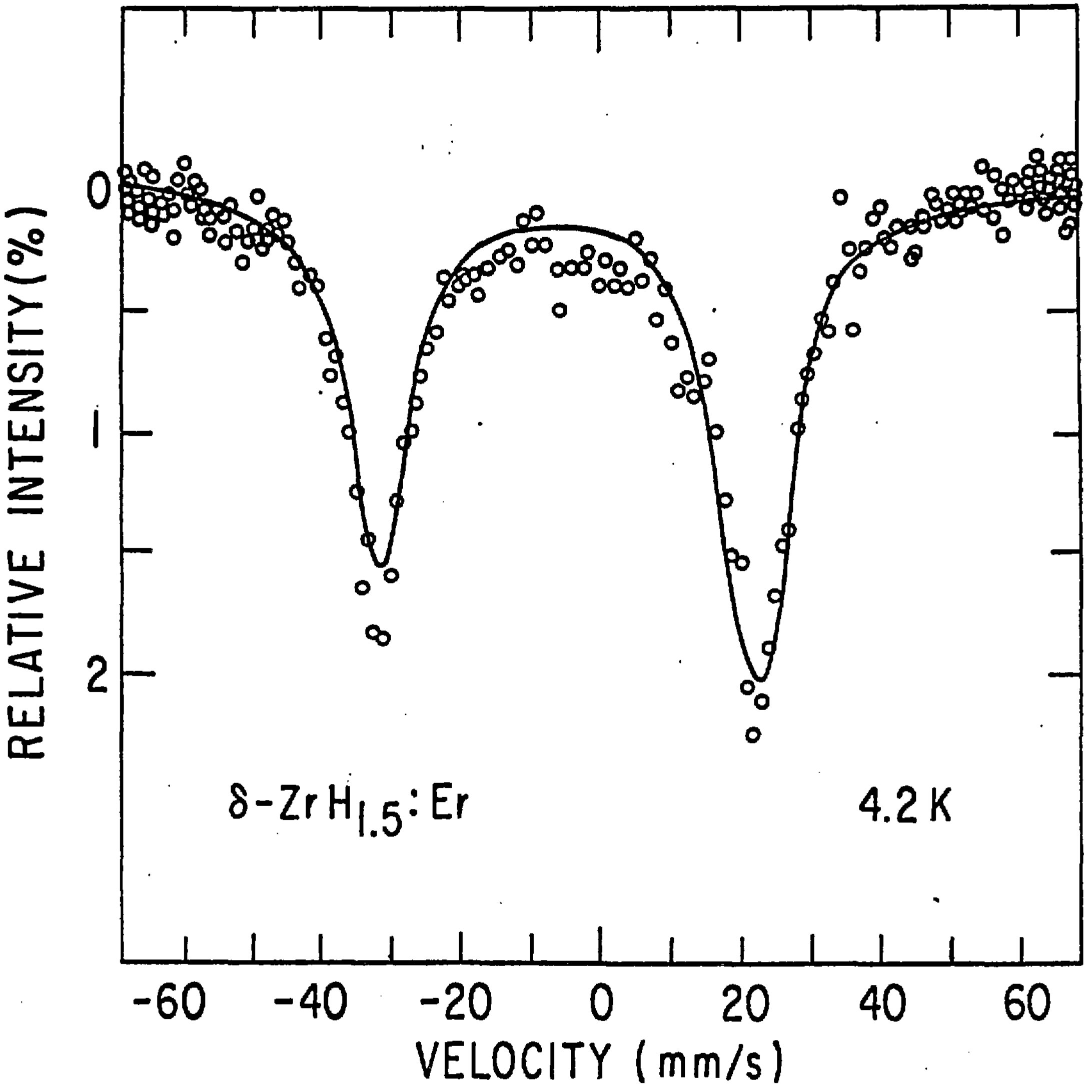
Fig. 1



K+E 10 X 10 TO THE CENTIMETER 46 1510
10 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.



RELATIVE INTENSITY (%)
0
1
2
-60
-40
-20
0
20
40
60
VELOCITY (mm/s)
δ-ZrH1.5:Er
4.2 K

Fig. 2

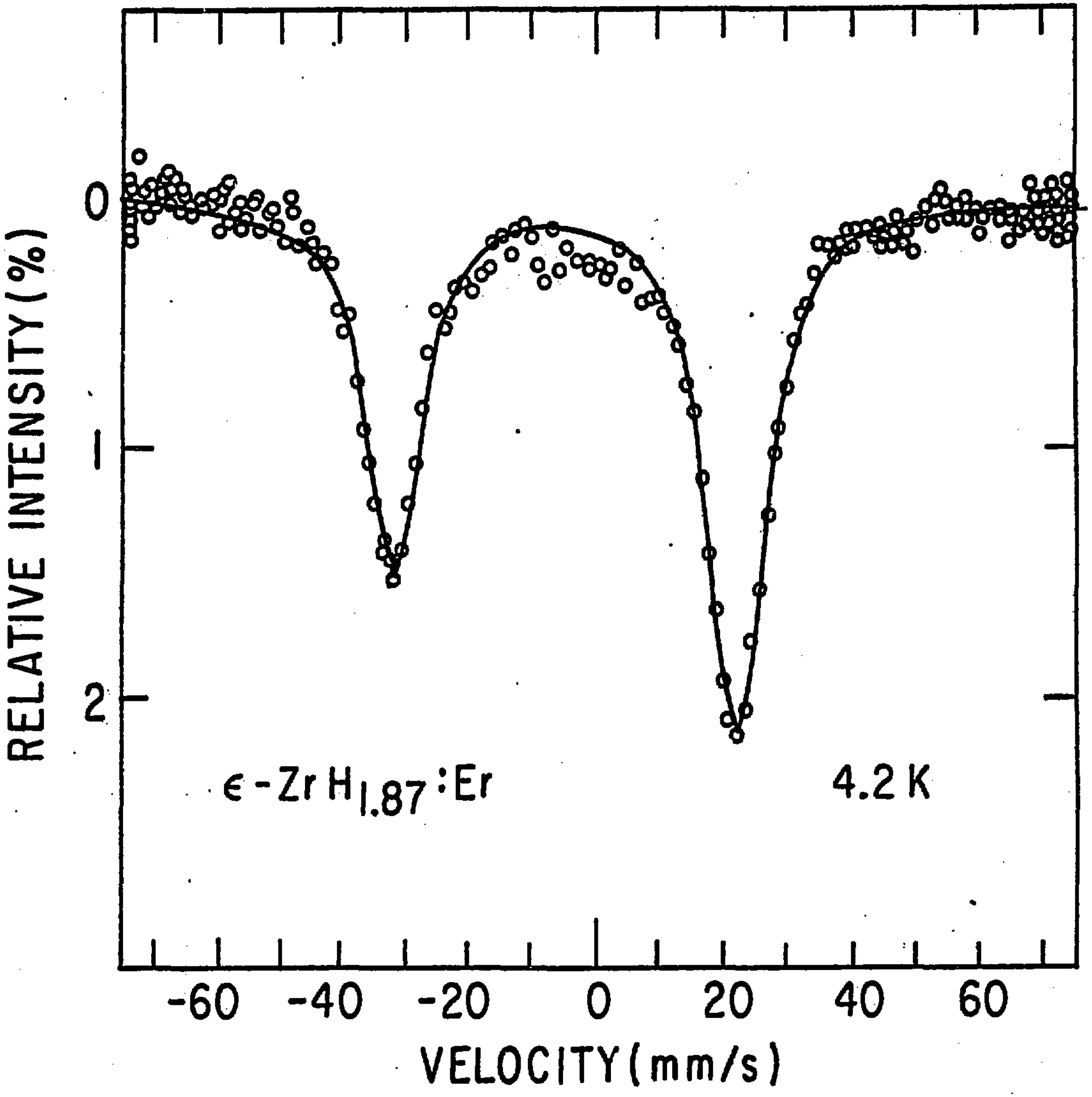

RELATIVE INTENSITY (%)
0
1
2
$\epsilon$-ZrH$_{1.87}$:Er
4.2 K
-60
-40
-20
0
20
40
60
VELOCITY (mm/s)

Fig. 3

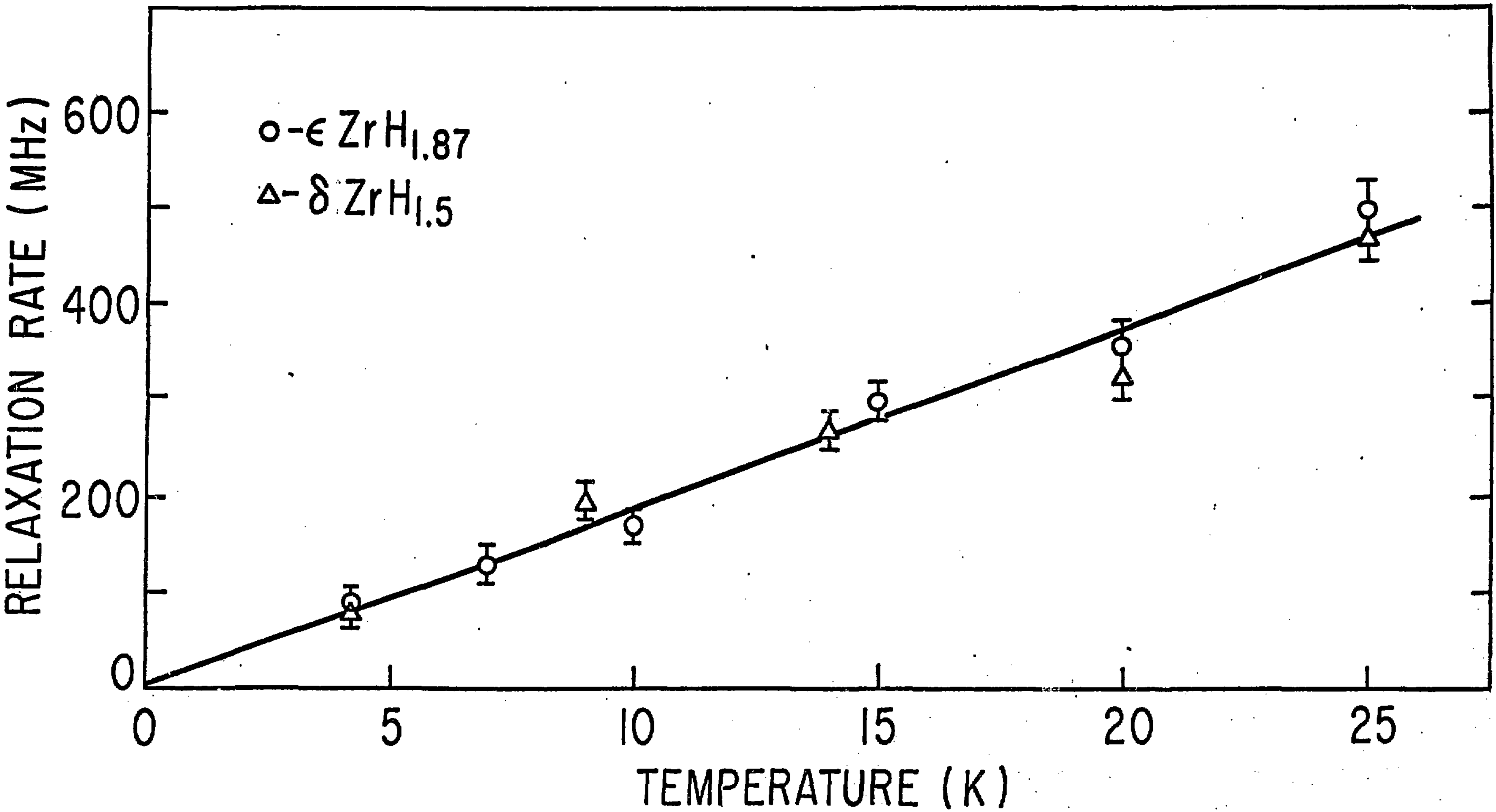

○ - ε ZrH1.87
△ - δ ZrH1.5
RELAXATION RATE (MHz)
0
200
400
600
0
5
10
15
20
25
TEMPERATURE (K)

Fig. 4