ESR DETECTION OF HYDROGEN SUPERSTRUCTURE IN THE HYDRIDE ZrV_2H_4

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Electron Spin Resonance experiments on Gd and Er ions diluted in ZrV_2H_x hydrides ($0 \leq x \leq 5$) were carried out at low temperatures between 1.5K and 4.2K. Hydrides were prepared by exposing cubic C15 ZrV_2 powders to hydrogen pressures of few atmospheres.

Let us briefly summarize our ESR results for ZrV_2H_x:No ERS spectra for either Gd or Er ions were observed for low hydrogen concentrations ($x \leq 2$) including the pure compound ($x=0$). This can be understood in terms of a structural cubic-to-rhombohedral phase transition that was seen to occur in the pure ZrV_2[1]. The low temperature rhombohedral phase would persist for low hydrogen concentrations ($x \leq 2$).For high hydrogen concentrations ($x > 2$)the Gd ESR line was observed and the ESR parameters were measured. Within the experimental error, the Gd g-value (2.04 ± 0.02) and Korringa rate $\Delta H/T$= (2.0 ± 0.5) G/K were found to be indepen-dent of the hydrogen concentration.

The positive g-shif (Δg = + 0.047) observed in the hydrides with respect to the g-value of 1.993 for Gd ions in insulators clearly indicates that the character of the conduction electrons is predominantly s-like in ZrV_2H_x.Since it is well known that ZrV_2 is a strongly d-band coumpoud (high density of d states at the Fermi level) our results show evidence of a drastic reduction of $N(E_F)$ in the ZrV_2 compound upon hydrogenation. This feature is in qualitative agreement with recent specific heat data obtained for ZrV_2 and $ZrV_2H_{1.5}$ by Geibel et al[2]. These authors have explained the substantial reduction of the specfic heat constant, $\gamma(ZrV_2) \simeq$ 16.2 mJ/K g-at; $\gamma(ZrV_2H_{1.3}) \simeq$ 3mJ/K^2 g-at, in terms of the protonic filling band model according to which the absorbed hydrogen atoms is assumed to deliver their electrons to the conduction bands of the ZrV_2 lowering $N(E_F)$. On the other hand, the Er resonance was observed in ZrV_2H_4 only. The average g-value (6.70 ± 0.10) measured in the temperature range $1.5K \leq T \leq 4.2K$ was found to be close to the theoretical Γ_7 ground state g-factor (6.78) of Er^{3+} ions in a cubic crystal field. Assuming a superstructure of hydrogen ions located at the 16(2Zr,2V) interstitial sites of the ZrV_2 lattice and assuming also that the Er ions are substitutional for Zr, we have calculated the crystal field parameters B_4, B_6 using the PCM model. This calculation leaves to a Γ_7 ground state for Er^{3+} in ZrV_2H_4. The Lea-Leask-Wolff parameter x was also calculated and its value ($x = -0.095$) implies a effective negative charge at the hydrogen ions tetrahedrally distributed around the Er ions. This provides strong evidence for the anionic hydrogen model in the ZrV_2H_x hydrides.

In summary, our experimental data and calculation seem to confirm the existence of a hydrogen atoms superstruture in the ZrV_2H_4 at low temperature. However the anionic hydrogen model for ZrV_2H_4 as evidenciated here contrasts with the protonic filling band model proposed by Geibel et al.[2] to explain the specific heat data on these hydrides. In our opinion, the elucidation of this discrepancy will require further experimental investigations as well as band structure calculation on ZrV_2H_x hydrides.

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2. C. Geibel, W. Galdacker, H. Keiber, V. Oestreich and H. Wühl, Phys.Rev. B, 30,11,6363 (1984)

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