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Impurity trapping in the Laves phase HfV_2 detected by perturbed angular correlations

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Abstract. A perturbed $\gamma\gamma$ angular correlation (PAC) study of the electric quadrupole interaction (QI) of ^{111}Cd probes on substitutional V sites in the C15 Laves phase HfV_2 has revealed a pronounced thermal hysteresis of the QI and the ^{111}Cd fraction on regular V sites: when samples are cycled through 700 K in vacuum, the quadrupole frequency ν_Q on the way down is found to be systematically larger than that on the way up at the same temperature. Simultaneously a sharp irreversible drop of the regular site fraction occurs upon cooling from 700 K. This behaviour indicates that HfV_2 reacts with water vapour at $T \leq 700$ K, dissociating residual H_2O into its atomic components. HfV_2 acts as a strong getter for the hydrogen, which is absorbed upon cooling below 700 K and again desorbed at $T > 800$ K. The oxygen, however, is absorbed only in trace amounts. These conclusions are supported by a mass spectroscopic desorption measurement and a comparative PAC study of the QI in the hydride $\text{HfV}_2\text{H}_{0.1}$, for which the activation energy for the hydrogen diffusion has been determined to be $E_a = 0.070(25)$ eV.

1. Introduction

The cubic C15 Laves phases ZrV_2 and HfV_2 have been extensively investigated in recent years because of their interesting superconducting and electronic properties on the one hand (Lawson 1971, Lawson *et al* 1972, Hafstrom *et al* 1978, Takei *et al* 1985, Lüthi *et al* 1985) and their pronounced hydrogen storage capacity on the other hand (Pebler *et al* 1967, Duffer *et al* 1976, Didisheim *et al* 1980, Irodova *et al* 1981).

Valuable contributions to the present state of knowledge on these compounds have been provided by hyperfine spectroscopic techniques. The electronic structure and its changes upon hydrogenation have been investigated by NMR measurements of Knight shifts and relaxation rates (Shinar 1984, Shinar *et al* 1984, Däumer *et al* 1988, Stepanov *et al* 1989). Activation energies and jump rates of the hydrogen diffusion in ZrV_2 and HfV_2 hydrides have been determined mainly by NMR (Shinar *et al* 1984, Däumer 1988). The occupation of the hydrogen sites in ZrV_2H_x has been studied by measurements of muon spin precessions (Hempelmann *et al* 1989).

The electric quadrupole interaction (QI) in ZrV_2 and HfV_2 and some of their hydrides has been investigated by ^2D and ^{51}V NMR (Saji *et al* 1972, Peretz *et al* 1981, Ding *et al* 1982, Belyaev *et al* 1984, Belyaev *et al* 1986) and by the ^{181}Ta perturbed angular correlation (PAC) technique (Jain and Saad 1983a, b, Heidinger *et al* 1983). These studies, aiming at information on the low temperature structural instability of these compounds

and the effect of hydrogenation on the electric field gradient, were mostly performed at or below room temperature and data on the quadrupole interaction at higher temperatures were not available.

Recently, however, the temperature dependence of the QI at the V site in HfV_2 was studied by ^{111}Cd PAC spectroscopy in the range $20 \text{ K} \leq T \leq 900 \text{ K}$ (Jain *et al* 1989) and a surprising anomaly was observed. The quadrupole frequency was found to increase with increasing temperature, in contrast to what is found in practically all metallic systems investigated up to now, where—due to thermal vibrations and lattice expansion—the quadrupole frequency decreases with increasing temperature (Vianden 1987).

This observation motivated further PAC investigations of the QI in HfV_2 , in order to test different models proposed as an explanation of the anomaly. In the course of these measurements we detected an unexpected hysteresis of the quadrupole frequency and the fraction of $^{111}\text{Cd}/^{111}\text{In}$ probes on substitutional V sites, when samples were cycled in vacuum through high temperatures. Mass spectroscopic desorption measurements on these samples and a comparative PAC study of the QI in the low concentration hydride $\text{HfV}_2\text{H}_{0.1}$ helped to relate this hysteresis to the trapping of hydrogen and oxygen impurities, provided most probably by the thermal dissociation of residual water molecules at the surface of HfV_2 . These measurements are the subject of the present paper.

2. The perturbed angular correlation (PAC) technique

The PAC technique is a hyperfine spectroscopic method which exploits the fact that γ -rays emitted from an aligned ensemble of excited nuclear states usually have an anisotropic intensity distribution. The Larmor precession of nuclear spins in extranuclear fields changes the alignment of the ensemble with time, and therefore hyperfine interactions (HFI) can be studied by observing the resulting time dependence of the γ -ray anisotropy. The initial alignment can be produced either by populating the excited states in a nuclear reaction or in the decay of radioactive nuclei by detecting those γ -rays which populate the excited states in the direction of the quantization axis. For details the reader is referred to Frauenfelder and Steffen (1965).

The time dependence of the anisotropy caused by the HFI can be expressed by perturbation factors $G_{kk}(t)$, which depend on parameters like multipole order, symmetry and time dependence of the interaction. In this investigation we are mainly concerned with static electric quadrupole interactions (QI) between the electric quadrupole moment Q of a nuclear state and the tensor V_{ij} of the electric field gradient (EFG) produced by the distribution of charges surrounding the nucleus under consideration. For a static QI and nuclear spin $I = 5/2$ in polycrystalline samples the perturbation factor $G_{22}(t)$ can be written as

$$G_{22}(t) = \sigma_{20} + \sum_{n=1}^3 \sigma_{2n} \cos(\omega_n t) \exp(-\frac{1}{2}\omega_n^2 \delta^2 t^2). \quad (1)$$

The frequencies ω_n in this expression are the transition frequencies between the 3 hyperfine levels into which a nuclear state with $I = 5/2$ is split by a QI. These frequencies depend on the two quantities which characterize the QI, the quadrupole frequency ν_Q and the asymmetry parameter η , defined as:

$$\nu_Q = eQV_{zz}/h \quad (2)$$

$$\eta = |V_{xx} - V_{yy}|/V_{zz}. \quad (3)$$

V_{xx} , V_{yy} and V_{zz} are the principal axis components of the EFG tensor with $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$. The exponential factor in the perturbation factor (equation (1)) accounts for possible distributions of the interaction frequencies caused by lattice imperfections, impurities and defects. The parameter δ is the relative width of a Gaussian distribution.

Frequently, several fractions f_i of nuclei with different QI parameters ν_{Qi} , η_i , δ_i are found in the same sample and the perturbation factor is then given by the superposition:

$$\overline{G_{22}(t)} = \sum_i f_i G_{22}(t; \nu_{Qi}, \eta_i, \delta_i). \quad (4)$$

PAC spectra can also provide information on time dependent interactions, such as the fluctuating QI produced by diffusing hydrogen atoms. In this case the perturbation of the angular correlation is most appropriately described by Blume's stochastic theory (Blume 1968). Under certain conditions, approximations of this complex theory can be used. For fast fluctuations, where the average residence time τ between diffusion jumps is much shorter than the nuclear precession period, the perturbation is well described by the following expression (Winkler and Gerdau 1973, Baudry and Boyer 1987):

$$G_{kk}(t) = \exp(-\lambda_k t) G_{kk}^{\text{stat}}(t). \quad (5)$$

From this relation one expects—for fast fluctuations—PAC spectra with exponentially damped oscillation amplitudes. For fluctuating QI of strength ν_Q^f and nuclear spin $I = 5/2$, the relaxation parameter λ_2 is given by $\lambda_2 = 2.487 (\nu_Q^f)^2 \tau$. This relation shows that the faster the fluctuations, the more the PAC spectrum tends towards a pattern with unattenuated oscillation amplitudes, corresponding to the motional narrowing of a NMR line.

$G_{kk}^{\text{stat}}(t)$ is the static perturbation factor for the time averaged interaction (Winkler and Gerdau 1973), which may include the effects of distributions of the static interaction (see equation (1)).

3. Experimental details

The PAC measurements were carried out with the 172–247 keV cascade of ^{111}Cd , which is populated in the EC decay of the 2.8 d isotope ^{111}In . This cascade is particularly well suited for PAC studies because of its strong intensity, the large anisotropy ($A_{22} = -0.17$, $A_{44} \sim 0$), and the favourable half-life ($T_{1/2} = 84$ ns) and relatively large quadrupole moment ($Q = 0.83$ b) (Herzog *et al* 1980) of the $I = 5/2$ state at 247 keV. The PAC spectra were recorded with a four-detector set-up, equipped with fast BaF_2 scintillators. Sample temperatures $T < 290$ K were obtained with a closed-cycle He refrigerator. Temperatures $T > 290$ K were obtained by resistance heating in a vacuum of 10^{-5} Torr. The temperature stability was better than 0.5 K.

Radioactive samples of HfV_2 doped with about 1 ppm of ^{111}In were produced by electron gun melting of metal foils of the constituents, onto which the radioactivity had been dropped from a commercially available solution of $^{111}\text{InCl}_3$. In one case, first an inactive sample of HfV_2 was produced by induction melting, which was then doped by electron gun melting with ^{111}In . The vacuum in the electron gun was of the order of 10^{-5} Torr. These samples were studied by PAC without prior annealing treatment. Typical data collection times were between 10 and 20 hours for each temperature. X-ray diffraction spectra of undoped, non-radioactive HfV_2 confirmed a single phase C-15 Laves structure with a lattice parameter $a = 7.39$ Å at 290 K, which is in good

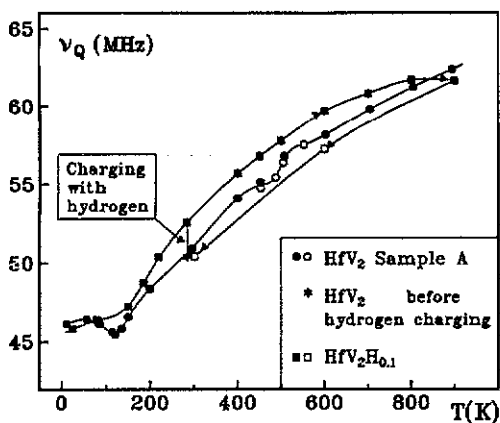


Figure 1. The electric quadrupole frequency ν_Q of ^{111}Cd in HfV_2 (sample A) and $\text{HfV}_2\text{H}_{0.1}$ as a function of temperature. Full points obtained by increasing temperatures, open points obtained upon cooling from 900 K.

agreement with the values reported in the literature (Duffer *et al* 1976, Heidinger *et al* 1983, Shinar *et al* 1984, Däumer *et al* 1988).

4. PAC measurements of ^{111}Cd in HfV_2

The QI of ^{111}Cd in HfV_2 has been investigated as a function of temperature in 3 different samples. The first of these samples (sample A) was produced by doping previously prepared inactive HfV_2 , the other samples were made by electron gun melting of the metal constituents with ^{113}In . For each temperature, the number of different fractions, their relative intensities f_i and QI parameters ν_{Q_i} , η_i , δ_i were determined by fitting equation (4) to the measured spectra.

4.1. ^{111}Cd in HfV_2 —sample A

The results of the first investigation of the QI of ^{111}Cd in HfV_2 —here called sample A—have been published by Jain *et al* (1989). For the later discussion of the effects observed with samples B and C, it is useful to summarize here the main results of the first investigation.

At all temperatures the measured PAC spectra could be well described by a single site. Practically all probe nuclei ($f_1 \geq 0.90$) are subject to the same well defined ($\delta \leq 0.03$) QI, which for $T > 120$ K has axial symmetry ($\eta \leq 0.1$). Both the symmetry and the strength of the interaction (see arguments by Jain *et al* (1989)) show that this site corresponds to ^{111}Cd occupying substitutional V sites. In the following it shall be called the regular site. The values of ν_Q and f_1 at 290 K are given in table 1.

The temperature dependence of the quadrupole frequency ν_Q is shown in figure 1. These data clearly reflect the lattice transition from orthorhombic to cubic symmetry, which in HfV_2 occurs at 120 K. In the cubic phase ν_Q increases with increasing temperature, with a change of slope and a slight indication of a discontinuity around 500 K. As a possible explanation of the increase of ν_Q with temperature Jain *et al* (1989) have suggested a combined effect of soft phonon modes and the recoil of the probe nuclei due to γ -ray emission.

Table 1. The quadrupole frequency $\nu_Q(290\text{ K})$ and the fraction $f_1(290\text{ K})$ of ^{111}Cd on substitutional V sites in samples of HfV_2 and $\text{HfV}_2\text{H}_{0.1}$ at room temperature as a function of the thermal history.

Sample	Thermal history	ν_Q (MHz)	Fraction f_1
HfV_2 —A	As prepared	51.0(2)	≥ 0.9
HfV_2 —B	As prepared	50.3(2)	≥ 0.9
	After 700 K	54.6(3)	0.3(1)
	After remelting	50.7(2)	≥ 0.9
HfV_2 —C	As prepared	50.4(2)	≥ 0.9
	After 700 K	53.1(3)	0.65(5)
	After 820 K—30 min	53.1(3)	0.65(5)
	After 900 K—2 days	50.7(2)	0.65(5)
$\text{HfV}_2\text{H}_{0.1}$	Before charging	50.3(2)	≥ 0.9
	Charged	52.6(2)	≥ 0.9

4.2. ^{111}Cd in HfV_2 —samples B and C

For a confirmation of the trends observed with sample A two more samples of HfV_2 (samples B and C), prepared by electron gun melting in high vacuum and unannealed, were investigated between 290 K and 700 K. At 290 K both samples showed a single-site PAC spectrum with the same parameters as sample A ($\eta \leq 0.1$, $\delta \leq 0.03$). The values of ν_Q and the fraction f_1 at 290 K are given in table 1, those obtained with sample B at higher temperatures are collected in figure 3, where the arrows indicate the thermal history of the sample.

It can be seen that again the quadrupole frequency increases upon heating. Up to 600 K the increase is almost linear and there is—if at all—only a very slight indication of a discontinuity at 500 K. Figure 2(a) shows the PAC spectrum measured at 700 K, the highest temperature reached with this sample. This spectrum is well described by a single site with the parameters: $\nu_Q = 59.7(2)$ MHz, $\eta \leq 0.10$, $\delta \leq 0.03$ and $f_1 \geq 0.9$.

Drastic changes of the PAC spectrum were observed, when in the next step the sample was cooled from 700 K to 520 K. The fraction f_1 of probe nuclei on regular sites decreased by almost a factor of 3 and simultaneously the regular site quadrupole frequency increased by more than 10%, compared to the value measured when the sample first passed through 520 K. These changes turned out to be irreversible, when the compound was heated back to 700 K. The PAC spectrum observed at 700 K after cooling to 520 K is shown in figure 2(b).

The comparison between figures 2(a) and (b) shows the remarkable effect of cooling to 520 K. The amplitude of the periodic oscillations of the anisotropy decreases strongly, reflecting the decrease of the number of probe nuclei on regular sites. However, the facts that the periodicity of the pattern is not affected and that the amplitudes of the maxima—although reduced—remain constant in time, indicate that for those probes remaining on regular sites the QI—now stronger than before cooling to 520 K—is still axially symmetric ($\eta \sim 0$) and sharply defined ($\delta \sim 0$). The description of the spectra now requires at least two fractions: the reduced regular site fraction ($\eta \sim 0$, $\delta \sim 0$) and a second 'irregular site' fraction which is characterized by a large frequency distribution.

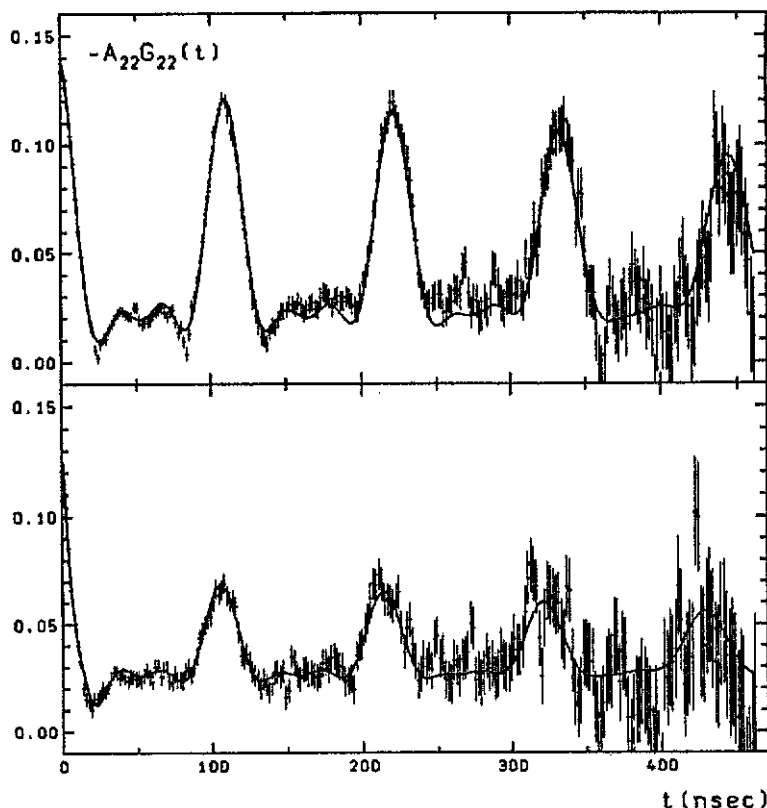


Figure 2. The perturbation factor $A_{22}G_{22}(t)$ of the angular correlation of ^{111}Cd in HfV_2 at 700 K (sample B). (a) Upper part: PAC spectrum at 700 K, obtained after continuous increase of the sample temperature. (b) Lower part: PAC spectrum at 700 K, after a previous temperature reduction to 520 K.

From 700 K the source was cooled in several steps to room temperature. The values of the regular site frequency ν_Q and fraction f_1 observed on the way to lower temperatures are shown in figure 3. This path is well separated and lies above the path followed on the way up to higher temperatures. Table 1 shows that when the sample is cycled once through 700 K, the regular site fraction at 290 K drops to a third of its initial value, while the frequency increases by roughly 10%. The irregular site is characterized by the following QI parameters: $\nu_Q = 135(10)$ MHz, $\eta \leq 0.2$, $\delta \sim 0.40$, $f_2 = (1 - f_1) = 0.7$.

The source was then remolten with the electron gun in a vacuum of 10^{-5} Torr and the PAC was measured again at 290 K. After remelting the original, single-site spectrum (parameters see table 1) was recovered. Then the sample was heated once again—but in one step—to 700 K. The regular site fraction remained unchanged ($f_1 \geq 0.9$), but the frequency at 700 K was now considerably lower ($\nu_Q = 58.4(2)$ MHz) than before, and when the sample was cooled back from 700 K to 520 K, no hysteresis effect was observed: the number of probe nuclei on regular sites remained high ($f_1 \geq 0.9$), and the frequency returned to the value measured on the way up. This clearly shows that the hysteresis effect depends on the time for which the sample is kept at high temperatures.

The same hysteresis effect was observed with sample C: the regular site fraction decreased and the frequency at 290 K increased after cycling once through 700 K (see

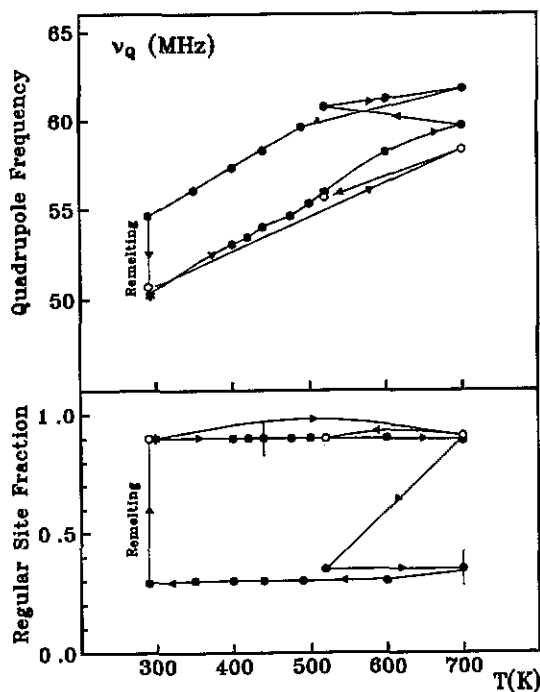


Figure 3. The quadrupole frequency ν_Q (upper part) and the relative fraction (lower part) of ^{111}Cd probes on substitutional V sites in HfV_2 (sample B) as a function of temperature. The arrows describe the thermal history of the sample. The asterisk denotes the start of the experiment.

table 1). Sample C was then transferred to a mass spectrometer and mass spectra were recorded, while the sample temperature was slowly raised. At about 820 K the desorption of hydrogen from the sample could clearly be detected by the strong increase of the hydrogen peak, relative to the reference spectrum of the unloaded mass spectrometer. The sample was kept for about half an hour at this temperature. Desorption of other gases was not observed. As shown by a PAC spectrum subsequently taken at 290 K, this desorption study had no effect on the quadrupole frequency and the regular site fraction, which remained at $\nu_Q = 53.1(3)$ MHz and $f_1 = 0.65$.

However, after keeping sample C for 2 days at 900 K in a vacuum of 10^{-5} Torr, the regular site fraction and the frequency at 290 K behaved quite differently: the fraction f_1 remained reduced to $f_1 \sim 0.65$, but the frequency returned to its initial value of $\nu_Q = 50.7$ MHz (see table 1). This clearly indicates that the changes of the quadrupole frequency and those of the regular site fraction induced by thermal cycling must have different causes. From the fact, however, that these changes appear simultaneously, it can be concluded that they are triggered by the same mechanism.

5. PAC of ^{111}Cd in $\text{HfV}_2\text{H}_{0.1}$

The cubic Laves phases HfV_2 and ZrV_2 are known to easily absorb large quantities of hydrogen without changing their lattice structure. At 290 K and 1 bar of H_2 pressure the hydrogen concentration of HfV_2H_x can reach values as high as $x \sim 3.8$.

^{51}V NMR measurements on HfV_2H_x have shown that the absorption of H strongly increases the QI at the V site (Ding *et al* 1982). The mass spectrometer analysis of the gases desorbed from sample C of HfV_2 at high temperatures revealed the presence of

hydrogen (see section 4.2). This raised the question of whether the hysteresis effects in samples B and C—increase of the regular site frequency, decrease of its fraction—are in some way related to an absorption of hydrogen.

We therefore investigated the effect of a small hydrogen concentration on the ^{111}Cd QI in HfV_2 . For this purpose a ^{111}Cd doped sample, prepared as before by electron gun melting, was charged with hydrogen to the concentration $\text{HfV}_2\text{H}_{0.1}$ by exposing the sample at 500 K to a corresponding quantity of H_2 gas.

PAC spectra of the hydrogenated sample were taken between 25 K and 900 K in a temperature sequence indicated by the arrows in figure 1. For these measurements, the sample was kept in a vacuum of 10^{-5} Torr. At all temperatures, including those reached by cooling from 700 K and 900 K, respectively, the spectra could be well described by axial symmetry ($\eta \sim 0$) and a single fraction $f_1 \geq 0.9$.

The attenuation of the oscillation amplitudes with time, however, was stronger than in the PAC spectra of uncharged HfV_2 . For $185 \text{ K} < T < 600 \text{ K}$ the attenuation decreases with increasing temperature towards a small value ($\delta \sim 0.007(1)$) which is constant above 600 K. This temperature dependence suggests that two effects contribute to the damping: a time dependent QI due to the diffusion of the hydrogen atoms—which is the faster the higher the temperature—and a weak distribution of the static part of the QI. The measurements were therefore analysed by fitting equation (5) to the spectra, assuming a temperature independent width of the static frequency distribution, which we deduced from the attenuation of the high temperature spectra.

Figure 4 shows the relaxation parameter λ_2 on a logarithmic scale as a function of the inverse temperature $1/T$. Above 200 K λ_2 and thus the average residence time τ decreases exponentially with increasing temperature, as expected for a thermally activated diffusion process. From these data (solid line in figure 4) one obtains $E_a = 0.070(25)$ eV for the activation energy of hydrogen jumps in $\text{HfV}_2\text{H}_{0.1}$. The relatively large error accounts for possible uncertainties coming from the assumption of a temperature independent width of the static frequency distribution. Our value for the activation energy in $\text{HfV}_2\text{H}_{0.1}$ is in good agreement with the results of proton NMR studies in $\text{HfV}_2\text{H}_{0.5}$ and the isomorphous compound ZrV_2H_x at small hydrogen concentrations ($x \leq 0.5$) (Shinar *et al* 1984).

Concerning the question of main interest in the context of this paper—the effect of hydrogen on the QI—we found that, as in the case of ^{51}V , the quadrupole frequency of ^{111}Cd increases, when hydrogen is absorbed by HfV_2 : at 290 K the increase is of the order of $\Delta\nu_Q/\nu_Q \sim 4.5\%$, from $\nu_Q = 50.3(2)$ MHz before charging to $\nu_Q = 52.6(2)$ MHz in $\text{HfV}_2\text{H}_{0.1}$.

In figure 1 the temperature dependence of the ^{111}Cd quadrupole frequency in hydrogenated $\text{HfV}_2\text{H}_{0.1}$ is compared to that of uncharged HfV_2 (data of sample A, section 4.1). As in HfV_2 , ν_Q in $\text{HfV}_2\text{H}_{0.1}$ increases with increasing temperature and as long as the sample is not heated beyond 800 K, the frequency of the hydrogenated compound is systematically larger by 4–5% than that of the uncharged sample. When, however, $\text{HfV}_2\text{H}_{0.1}$ is cooled from 900 K, one obtains—at 600 K and 290 K—the frequency of uncharged HfV_2 . This indicates that desorption of hydrogen sets in at $T > 800$ K, in agreement with the thermal hydrogen desorption spectra of HfV_2H_x by Stern *et al* (1982), which at low concentrations x show a single peak at about 900 K.

It is worthwhile to mention at this point, that at high hydrogen concentrations the temperature dependence of the ^{111}Cd QI in HfV_2 hydrides shows no anomaly: in HfV_2H_4 the ^{111}Cd quadrupole frequency was found to decrease with increasing temperature (Forker *et al* 1989). HfV_2 is characterized by a high density of electronic states $N(E_f)$.

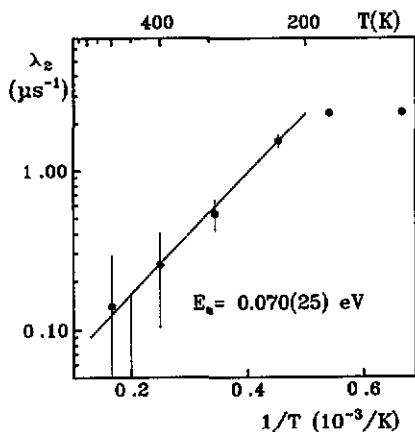


Figure 4. The parameter λ_2 of the quadrupole relaxation of ^{111}Cd in $\text{HfV}_2\text{H}_{0.1}$ versus the inverse temperature $1/T$.

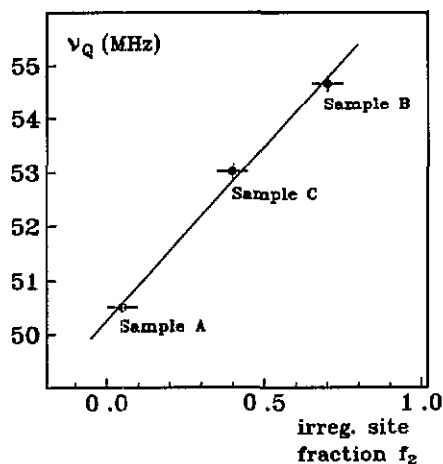


Figure 5. The regular site quadrupole frequency $\nu_Q(290\text{ K})$ of ^{111}Cd in HfV_2 , obtained after cycling the samples through high temperatures, versus the relative fraction of ^{111}Cd probes subject to a large frequency distribution (irregular site fraction f_2) in samples A, B and C.

The shift of the Fermi energy E_f upon hydrogen absorption, however, leads to a strong decrease of $N(E_f)$ with increasing hydrogen concentration (Däumer *et al* 1988, Stepanov *et al* 1989). The fact that for HfV_2 $d\nu_Q/dT > 0$, but for HfV_2H_4 $d\nu_Q/dT < 0$ might therefore point towards some relation between the anomaly $d\nu_Q/dT > 0$ and the high density of $N(E_f)$ in HfV_2 . This aspect is presently under experimental investigation.

6. Discussion

The observation of a hydrogen peak in the desorption spectrum of sample C (see section 4.2) and the fact that $\nu_Q(\text{HfV}_2\text{H}_{0.1}; T) > \nu_Q(\text{HfV}_2; T)$ for $T < 800\text{ K}$ (see figure 1) leave little doubt that the increase of the regular site frequency of HfV_2 after cycling the sample through 700 K is due to the absorption of hydrogen.

A hydrogen contamination is also consistent with the observation that the initial value of the quadrupole frequency $\nu_Q(295\text{ K})$ is recovered after remelting or heating in vacuum to 900 K for 2 days, but not by heating to 820 K for 30 minutes (see table 1 and figure 3): in the first 2 cases the contamination is completely removed, in the last case time is too short for significant desorption and corresponding change of ν_Q .

From this observation—no change of $\nu_Q(290\text{ K})$ within $\Delta\nu_Q = 0.2\text{ MHz}$ after 30 minutes at 820 K—one estimates, using the frequency difference between HfV_2 and $\text{HfV}_2\text{H}_{0.1}$ $\Delta\nu_Q/\Delta x \sim 23\text{ MHz}$ as a calibration, an upper limit of the desorption rate at 820 K of $\Delta x/\Delta t \leq 5 \cdot 10^{-6}\text{ s}^{-1}$. At this rate, the desorption in 2 days would amount to $x \geq 1.0$.

The concentration of absorbed hydrogen can be estimated from the frequency increase $\Delta\nu_Q(295\text{ K})$ caused by cycling through 700 K. With $\Delta\nu_Q/\Delta x \sim 23\text{ MHz}$

one obtains $x \sim 0.19$ for sample B and $x \sim 0.12$ for sample C. This corresponds to $1-2 \times 10^{-5}$ moles of absorbed hydrogen (sample masses ~ 50 mg).

It has been reported that when samples of (Hf, Zr)V₂ are stored in air for periods of several months, some of their properties change due to the absorption of hydrogen from the atmosphere (Smith *et al* 1973, Balakin *et al* 1983). On the time scale of our experiments the atmosphere can be eliminated as possible hydrogen source. We found no difference in $\nu_Q(290\text{ K})$ of HfV₂ exposed at 290 K to the atmosphere for 300 hours and of the freshly prepared compound within $\Delta\nu_Q \sim 0.2$ MHz ($\Delta x \leq 0.01$).

Key elements for the identification of the hydrogen source are (i) the observation that an irregular site appears in the PAC spectra when hydrogen is absorbed by cycling the sample through 700 K, but not, when HfV₂ is charged to HfV₂H_{0.1} and (ii) the fact that the irregular site fraction f_2 grows with increasing concentration of the absorbed hydrogen. In figure 5 the regular site frequency $\nu_Q(290\text{ K})$ obtained after cycling through 700 K has been plotted versus the irregular site fraction f_2 of samples A, B and C. For low H concentrations x , ν_Q increases linearly with increasing x (Ding *et al* 1982, Peretz *et al* 1981). Consequently, the linear relation between $\nu_Q(290\text{ K})$ and f_2 in figure 5 implies that the irregular site fraction f_2 is directly proportional to the quantity of absorbed hydrogen.

So, while it is clearly not the hydrogen which causes the irregular site, its fraction f_2 grows with the quantity of absorbed hydrogen. This leads to the conclusion that a second contaminant must be involved in the occurrence of the irregular site, taken up in a constant proportion to the absorbed hydrogen, when the sample is cycled through 700 K.

A mechanism, which would provide a second contaminant in a constant proportion to the hydrogen contamination, is the dissociation of H₂O molecules at the hot surface of HfV₂ and the simultaneous absorption of both hydrogen and oxygen, when the sample is cooled down. The dissociation of about 200 μg of H₂O—provided by residual water molecules adsorbed on the walls of the vacuum vessel of the furnace—would be sufficient to produce the quantity of H₂ ($\sim 10^{-5}$ mol) necessary to account for the frequency increase in samples B and C.

It has been observed that ¹¹¹In probes in metallic environments may trap oxygen impurities and form stable In–O_x configurations (Pasquevich *et al* 1981). The QI parameters of these In–O_x complexes are very similar to those the irregular site appearing in samples B and C after cooling from 700 K: a broad frequency distribution with a relative width $\delta \sim 0.3$ and a centre frequency of the order of 100 MHz. Because of this similarity of the QI parameters, it appears a reasonable assumption—although it is no direct proof—to identify the irregular site fraction in HfV₂ with In–O_x complexes, formed by trapping of absorbed oxygen impurities.

The irregular site fraction f_2 is then proportional to the concentration of adsorbed oxygen, and since the regular site frequency $\nu_Q(290\text{ K})$ is a measure of the hydrogen concentration, it is clear that—as shown by the data in figure 5— ν_Q and f_2 must have the same ratio in any contaminated sample, if dissociating H₂O is the source of the contamination.

This identification would also fully explain the observation that while the increased regular site frequency can be restored to its initial value at 290 K both by heating to 900 K (sample C) and by melting (sample B), the full regular site fraction can only be recovered by melting. The temperature of 900 K is sufficient to desorb the rapidly diffusing hydrogen from the sample, but it obviously requires higher thermal energies to break the In–O bonds. Even if the In–O_x complexes are stable at the melting temperature of HfV₂ (T_M 1770 K), in the molten sample In–O_x can be expected to segregate

from the liquid metal phase. Upon rapid solidification the intermetallic compound is then free of contaminations and the regular site fraction reaches again its full value.

The concentration of the $^{111}\text{In}/^{111}\text{Cd}$ probes is of the order of a few ppm. If ^{111}In is accepted to act as an oxygen trap in HfV_2 , then the fact that a finite regular site fraction ($f_1 \sim 0.3$ in sample B) survives the thermal cycling, implies that the concentration of adsorbed oxygen must be of the same order as the In concentration, i.e. in the ppm range. The hydrogen concentration has been estimated above to be of the order of a few percent, which suggests that in this temperature range the absorption rates of HfV_2 for oxygen and hydrogen contaminants differ by roughly four orders of magnitude.

In sample A both the frequency and the regular site fraction were found to be fully reversible upon cooling (figure 1). This is probably due to several factors: one is the fact that sample A was heated to 900 K, where the desorption rate of low concentration HfV_2 hydrides has its maximum (Stern *et al* 1982) so that—as confirmed by sample C—complete desorption occurs during data collection at 900 K. But also, the reversibility might reflect better vacuum conditions for sample A. In fact, the hysteresis of the regular site frequency and fraction found in samples B and C can be suppressed by isolating the compound from the source of the contamination: the hysteresis effect never occurred, when in another context numerous samples sealed into small quartz capsules under high vacuum were investigated.

In summary, PAC spectroscopy has proved to be a highly sensitive tool for investigations of the interaction of metallic systems with gaseous impurities in minute concentrations. The measurements presented here indicate that the C15 Laves phase HfV_2 reacts with water vapour at temperatures $T \leq 700$ K, dissociating H_2O into its atomic components. HfV_2 acts as a strong getter for the hydrogen, which is absorbed when the compound is cooled below 700 K and again desorbed at temperatures $T > 800$ K. In the same temperature range, the oxygen, however, is absorbed only in trace amounts.

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