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Dynamics of lattice transformation in HfV_2

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Abstract. The 245 keV ($\frac{5}{2}^+$) state in ^{111}Cd has been used as a probe to study the lattice instability at the V site in the superconducting compound HfV_2. The temperature dependence of the electric quadrupole interaction frequency ω_0 has been understood by assuming the presence of soft-phonon modes, the γ-recoil effects and a small (about 1%) increase (decrease) in the charge at the V (Hf) site above the lattice transformation temperature $T_L \simeq 120$ K. A high-temperature phase transition has also been observed in HfV_2 at $T \simeq 520$ K.

1. Introduction

The lattice instability in the superconducting cubic Laves phase (C15) compounds has been studied (Jain and Saad 1983a, b, Heidinger *et al* 1983, Jain *et al* 1987) through the time differential perturbed angular correlation (TDPAC) experiments by observing the temperature dependence of the electric field gradient experienced by the ^{181}Ta probe occupying the cubic Hf site in the compounds (Hf, Zr)V_2. The lattice instability has been observed in these experiments through a dramatic change in the electric field gradient at the Hf site near the lattice transformation temperature. A more surprising observation has been the presence of a temperature-dependent electric field gradient at the cubic Hf site in the cubic phase of these compounds. This observation could be understood by assuming the appearance of soft-phonon modes near the lattice transformation temperature and the presence of the γ-recoil effect which induces transitions between the cubic and the orthorhombic phases of these compounds.

A further verification of these ideas could be provided through a study of the temperature dependence of the electric quadrupole interaction at the V site in these compounds. The V site has a non-cubic symmetry even in the cubic phase of the compound HfV_2 and was first studied through the NMR technique by Saji and Yamadaya (1972) who showed that the electric quadrupole coupling constant increased by a factor of about 2.5 from a value of $e^2qQ/h = 1.18 \pm 0.02$ MHz at 295 K to a value of 2.99 ± 0.2 MHz at 77 K. These results were later supported by Kozhanov *et al* (1979). However, the lattice sum calculations by Jain *et al* (1981) indicated a relatively small increase of about 6% in the electric field gradient at the V site in going from the cubic to the orthorhombic phase of the compound HfV_2. These calculations were supported by the NMR measurement performed by Ding *et al* (1982) with the compound HfV_2.

In view of the discrepancy between the NMR experiments, it was considered desirable

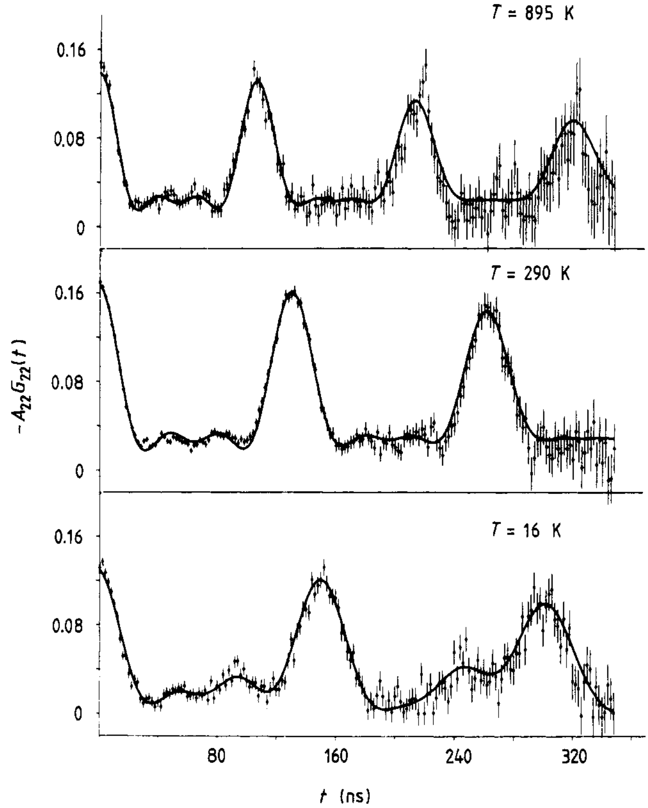

Figure 1. The angular correlation coefficients $A_{22}G_{22}(t)$ against time for the 172–245 keV γ–γ cascade in ^{111}Cd occupying the V site in the compound HfV_2 at $T = 16$ K, $T = 290$ K and $T = 895$ K.

to investigate the V site through a different but more sensitive technique. We report in this paper the study of the temperature dependence of the electric quadrupole interaction at the V site in the compound HfV_2 through the TDPAC method. The 245 keV ($I^{\pi} = \frac{5}{2}^{+}$, $T_{1/2} = 84.1$ ns) state in ^{111}Cd populated in the electron capture decay of ^{111}In was used as a probe for these studies.

2. Experimental procedure and results

The preparation of the compound HfV_2 has been discussed earlier by Jain *et al* (1981). The radioactive sources were prepared by first depositing about 2 mCi of ^{111}In activity onto a piece (of mass about 100 mg) of the compound HfV_2. This was dried under an infrared lamp and melted with the help of an electron gun under high vacuum. While the bulk of the activity evaporated during melting, a small fraction (about 2%) was trapped in the compound. This radioactive compound was used for the TDPAC measurements. A four-detector system with two fixed and two movable detectors and a fast–slow coincidence system with a time resolution 2τ of about 3.0 ns was used for measuring the TDPAC of the 172–245 keV γ–γ cascade. The coincidences were measured with the moving counters at 90°, 135° and 180° with respect to the fixed counters. A closed-cycle refrigerator was used for measurements below room temperature while a furnace with a temperature controller was used for temperatures above 295 K. The temperature stability was better than 0.5 K. The anisotropy against time for the 172–245 keV γ–γ cascade in ^{111}Cd was measured for temperatures ranging between 16 and 895 K. Figure 1 shows the plots of the angular correlation coefficient $A_{22}G_{22}(t)$ against time at three

Table 1. The temperature dependence of the electric quadrupole interaction frequency ω_0, the frequency distribution width δ and the asymmetry parameter η experienced by the ^{111}Cd probe at the V site in HfV_2. The downward arrow (↓) represents decreasing temperature; the upward arrow (↑) represents increasing temperature.

Sample 1					Sample 2				
Run	T (K)	ω_0 (MHz)	δ	η	Run	T (K)	ω_0 (MHz)	δ	η
9	16	43.45(16)	0.038(4)	0.208(8)	1	290 ↑	48.05(25)	0.044(6)	0
8	70	43.77(16)	0.039(4)	0.154(14)	2	400 ↑	51.00(20)	0.062(4)	0
7	90	43.50(10)	0.030(3)	0.133(22)	3	507 ↑	53.50(20)	0.055(4)	0
6	115	42.97(10)	0.025(3)	0.080(12)	4	602 ↑	54.70(15)	0.046(3)	0
5	120	42.87(5)	0.032(3)	0	5	704 ↑	56.40(20)	0.042(4)	0
4	135	43.19(10)	0.028(3)	0	6	800 ↑	57.75(15)	0.041(3)	0
3	150	43.93(10)	0.028(3)	0	7	895 ↑	58.80(20)	0.037(4)	0
2	200	45.57(10)	0.027(3)	0	8	551 ↓	54.15(15)	0.039(4)	0
1	290	48.05(5)	0.026(3)	0	9	452 ↓	51.70(15)	0.035(4)	0
10	290 ↑	48.43(16)	0.029(5)	0	10	486 ↓	52.35(15)	0.039(4)	0
					11	504 ↓	53.10(20)	0.043(4)	0
					12	453 ↑	52.05(25)	0.043(5)	0

temperatures $T = 16$ K, $T = 290$ K and $T = 895$ K. The experimental data were fitted by assuming the presence of a randomly oriented electric quadrupole interaction with a Gaussian frequency distribution described by the parameter δ, the distribution width in the electric quadrupole interaction frequency ω_0 and the asymmetry parameter η. The quadrupole frequency is given by $\omega_0 = 6eQV_{zz}/\hbar 4I(2I - 1)$ where I is the nuclear spin, Q the quadrupole moment of the nuclear state and V_{zz} the electric field gradient (EFG) at the nuclear site. The symmetry parameter is given by $\eta = |V_{xx} - V_{yy}|/V_{zz}$ where V_{xx} and V_{yy} are the x and y components of the EFG tensor in the principal-axes system. The values of ω_0, δ and η obtained from the fits to TDPAC spectra measured with two samples of HfV_2 in the temperature range between 16 and 895 K are presented in table 1. The arrows have been used to indicate the increasing (↑) or a decreasing (↓) temperature. The values obtained at room temperature are $\omega_0 = 48.05(25)$ Mrad s^{-1}, $\delta = 0.044(6)$ and $\eta = 0$ (sample 2). The presence of a single frequency with a small frequency distribution and a zero-asymmetry parameter indicates that the ^{111}Cd probe occupies a well defined and unique site in the HfV_2 lattice. The EFG experienced by the ^{111}Cd probe can be calculated from the measured value of ω_0 by assuming a value of $Q = 0.77 \pm 0.12$ for the quadrupole moment (Lederer and Shirley 1978) of the 245 keV ($\frac{5}{2}^+$) state in ^{111}Cd. The ratio of the measured EFG experienced by the ^{111}Cd and ^{51}V probe is found to be 2.8 ± 0.7. This is in reasonable agreement with the ratio of the Sternheimer anti-shielding factors (Feiok and Johnson 1969) $(1 - \gamma_\infty)_{^{111}Cd}/(1 - \gamma_\infty)_{^{51}V}$ which is equal to 3.44. It is reasonable to assume, therefore, that the ^{111}Cd probes are occupying well defined V sites in the compound HfV_2. The possibility of the ^{111}Cd probes occupying the cubic Hf sites can be ruled out because of a weak electric quadrupole interaction ($\omega_0 \simeq 0$) expected there. Since the ^{111}Cd probes are experiencing a symmetric electric quadrupole interaction with a single frequency and a small frequency distribution, it is unlikely that they are occupying an interstitial lattice site.

3. Discussion

The measurement of the electric quadrupole interaction frequency ω_0 as a function of

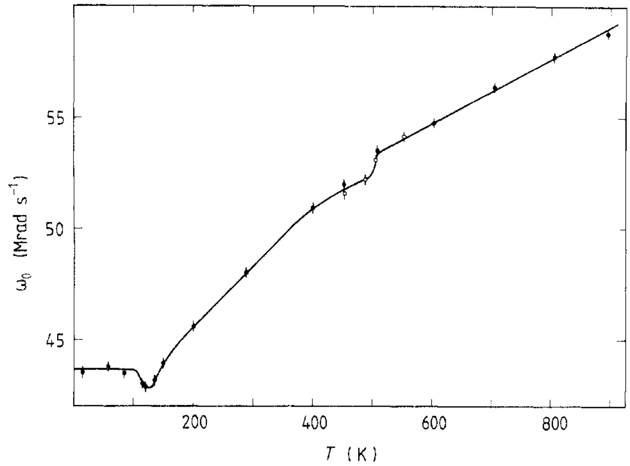

Figure 2. The electric quadrupole interaction frequency ω_0 as a function of temperature between 16 and 895 K: ○, obtained with decreasing temperature; ●, obtained with increasing temperature in sample 2. The ω_0-values obtained with decreasing temperature do not deviate from the ω_0-values obtained with increasing temperature.

temperature in the temperature range between 16 and 895 K is shown in figure 2. It shows some interesting features.

(i) The value of ω_0 shows a minimum at 120 K which is consistent with the lattice transformation temperature obtained from the bulk measurements and the observation of a sharp discontinuity in EFG at the Hf site (Jain and Saad 1983a, b, Heidinger *et al* 1983) in this compound.

(ii) The measured asymmetry parameter η is zero in the cubic phase at room temperature but increases slowly as the temperature is decreased below the lattice transformation temperature T_L. This is consistent with the lattice sum calculations (Jain *et al* 1981) and the symmetry considerations which require $\eta = 0$ because of axial symmetry at the V site at room temperature. This symmetry is destroyed at temperatures below the lattice transformation temperature. Hence, a non-zero value of η is expected. The measured value is $\eta = 0.18(5)$ at $T = 16$ K.

(iii) The value of the electric quadrupole interaction frequency ω_0 shows a steady increase with increasing temperature in the cubic phase of this compound. This is a rather surprising observation since ω_0 is normally found to decrease with increasing temperature because of the lattice expansion in pure metals or inter-metallic compounds. It might be possible to understand this behaviour by suggesting that the ^{111}Cd probe occupies interstitial positions rather than substitutional sites. For example, it might be on a site slightly displaced from the V site along the symmetry axis, and the displacement could change with temperature in such a way that the quadrupole interaction increases while η remains zero and δ also remains unchanged and close to zero. Also the EFG should be close to the value observed with a ^{51}V probe at the V site. Although possible, it looks improbable because we do not know of a mechanism or a force that will restrict the motion of the Cd impurities along the symmetry axis in only one direction so that the EFG experienced by them will increase with temperature.

If the ^{111}Cd probe is assumed to occupy regular V sites, the observed temperature dependence of ω_0 can be understood in terms of the presence of the soft-phonon modes (Jain and Saad 1983a, b) in the cubic phase of the HfV_2 lattice. The phonon vibrations give rise to a mean-square displacement of the atoms around their mean positions, leading to a distortion of the lattice. Normally, the amplitude of these vibrations is quite small. Therefore the distortion is not observable in the x-ray diffraction measurements.

However, the ^{111}Cd nuclei receive a recoil of the order of 150 meV (or 1700 K) owing to the emission of 172 keV γ-ray. The neutrino emission in the electron capture decay of ^{111}In also leads to the recoil of the ^{111}Cd nuclei with a wide range of energies depending on the energy of the neutrino emitted. This large recoil energy excites the phonon vibrations in the HfV_2 lattice with large amplitudes and gives rise to an observable distortion of the local symmetry in the neighbourhood of the ^{111}Cd probe. The distortion of the lattice is described in terms of the distortion parameter with values ranging from 0 to $\varepsilon(T)$ and determined from the softness or rigidity of lattice. In the cubic phase, the HfV_2 lattice becomes more rigid with increasing temperature. Therefore the mean-square distortion $\varepsilon^2(T)$ decreases with increasing temperature. If the EFG at the V site is larger in the cubic phase of HfV_2, the value of ω_0 should increase with increasing temperature in agreement with the observation.

The above behaviour can also be described in an alternative way. In this picture, the γ-recoil induces fast transitions from the cubic to the orthorhombic phase and vice versa in the local neighbourhood of the Cd probe above 120 K in HfV_2. The observed temperature dependence of the EFG is, therefore, obtained as a time average of the EFG in the cubic phase and a smaller EFG in the orthorhombic phase at the V site. It should be emphasised that we are talking about the fluctuation of the EFG at a single (V) site and a static time average is obtained because the rate of fluctuation is much faster than the time resolution of our experiment. This time average is decided by the relative mixing of the two phases. In the present case, the amplitude of the orthorhombic phase decreases with increasing temperature, thereby increasing the EFG with increasing temperature. In principle, it should be possible to obtain a rigid lattice with no γ-recoil effects at a sufficiently high temperature and to observe the quadrupole frequency corresponding to the pure cubic phase. Thereafter, ω_0 should remain constant or decrease with temperature—as expected for a rigid lattice—provided that there is no other phase transition in this temperature region. In the present experiment, we observe an increase in ω_0 right up to 870 K and the curve of ω_0 against T shows a kink and a subsequent change in the slope of this curve at $T > 520$ K. This is an indication of a high-temperature phase transition of HfV_2. This has been extensively studied by Forker *et al* (1989).

The present TDPAC spectra also show that the amplitude of oscillations is not appreciably reduced during the period of our observation. This indicates the absence of any relaxation effects and suggests that the lifetime of the phonon vibrations, induced by the γ-recoil effects, is longer than the period of our observation, i.e. $\tau_{phonon} > 330$ ns.

The measurements presented above indicate a higher value of the EFG at the V site in the cubic phase compared with the orthorhombic phase below 120 K in the compound HfV_2. The lattice sum calculations (Jain *et al* 1981), on the contrary, indicate an increase of about 6% in the orthorhombic phase at 80 K over the value in cubic phase at 298 K if a valence $Z_{Hf} = 4$ and $Z_V = 2$ is assumed for the Hf and V atoms, respectively. The observed increase in the EFG at the V site in the cubic phase of the comound HfV_2 can, however, be understood by assuming a small increase of about 1% in the charge at the Hf site or a similar decrease at the V site above the lattice transformation temperature T_L. This can happen if, for example, there is a shift in the Fermi level or a small (about 1%) transfer of charge from the Hf to the V site above the lattice transformation temperature T_L.

The anomalous temperature behaviour of ω_0 in HfV_2 was further confirmed by repeating the above measurements with the ^{111}In activity diffused in the compound $HfCo_2$ which has the same C15 cubic Laves phase structure but is not superconducting. The observed TDPAC patterns in $HfCo_2$ were fitted for a value of the quadrupole interaction frequency $\omega_0 = 0$ with the frequency distribution width $\Delta\omega_0 \simeq 5.0(2)$ Mrad s^{-1}. In addition, the values of ω_0 and $\Delta\omega_0$ were found to be constant over the entire temperature range. The value of $\omega_0 = 0$ indicates that the ^{111}Cd probe occupies the (cubic) Hf and not the (orthorhombic) Co site in $HfCo_2$. The above measurements also indicate that the cubic symmetry is maintained at the Hf site in $HfCo_2$ over the entire temperature range. In this situation, the quadrupole frequency at the Co site can change only owing to the expansion on heating, and contraction on cooling, the $HfCo_2$ lattice while maintaining the cubic symmetry at the Hf site. The lattice sum calculations indicate a 3% decrease in the EFG at the Co site when the lattice parameter a_c is increased from 7.37 to 7.40 Å in the cubic Laves phase compound $HfCo_2$. It is, therefore, not unreasonable to conclude from observation of a temperature-independent value of $\omega_0 = 0$ at the Hf site that the quadrupole frequency at the Co site (if it was occupied by the ^{111}Cd probe) will either be temperature independent or show a decrease with increasing temperature owing to expansion of the lattice. The measurements in $HfCo_2$ could, therefore, be used as a support to the view that the anomalous temperature dependence of ω_0 at the V site is related to the presence of superconductivity in HfV_2.

The results of the present experiment have thrown considerable light on the dynamics of the lattice transformation in HfV_2. They have provided evidence for the slow but steady softening of the lattice prior to the eventual collapse from the high-temperature (cubic) to the low-temperature (orthorhombic) phase. If the recoil effects are playing a significant role in the process discussed above, it is desirable to study the dependence of these effects on the recoil energy of the probe nucleus.

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