Impurity Quadrupole Interaction in Light Rare Earth Metals: ^{111}Cd in La, Pr and Nd *

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The nuclear quadrupole interaction of dilute ^{111}Cd impurities has been investigated in the light rare earth (RE) metals La, Pr and Nd by time differential perturbed angular correlation measurements. The quadrupole frequency ν_Q has been determined in Pr as a function of temperature and pressure, in Nd as a function of temperature, and in La at 19 K. The pressure dependence of ν_Q of ^{111}Cd in Pr $((\mathrm{d}\ln\nu_Q/\mathrm{d}P)_{290\,\mathrm{K}} = +2.7(2.3)\cdot 10^{-3}\,\mathrm{Kbar}^{-1})$ is a factor of 3–4 weaker than in the heavy RE metals Gd to Er. At the same time the temperature dependence of ν_Q in the light RE is up to a factor of 3 stronger than in the heavy RE. Between 300 K and 900 K the quadrupole frequency is a linear function of temperature with the same slope $(\mathrm{d}\ln\nu_Q/\mathrm{d}T)_{290\,\mathrm{K}} = -8.4(2)\cdot 10^{-4}\,\mathrm{K}^{-1}$ both in Pr and Nd. Between 25 K and 300 K the decrease is stronger than linear, and more pronounced in Pr than in Nd. The temperature coefficient $(\mathrm{d}\ln\nu_Q/\mathrm{d}T)_{290\,\mathrm{K}}$ is found to decrease linearly with the RE atomic number across both the series of the light and the heavy RE metals.

Introduction

The data presently available on the nuclear quadrupole interaction (NQI) in the heavy rare earth (HRE) metals Gd (4f^7) to Lu (4f^{14}) suggest that although the 4f electrons are well shielded and localized deeply inside the RE ion cores, they influence the electric field gradient (EFG) seen by an impurity on a substitutional host site to a considerable extent. Evidence for such an influence comes from the variation of the ratio $\alpha = V_{zz}/(1-\gamma_\infty)\,V_{zz}^{\mathrm{lat}}$ between the total EFG V_{zz} and its ionic part $(1-\gamma_\infty)\,V_{zz}^{\mathrm{lat}}$ [1, 2] and also of the temperature dependence of the EFG [3] with the number of 4f electrons.

It is interest to extend these impurity NQI studies to the light rare earth (LRE) metals, which reach from La (4f^0) to Eu (4f^7). The different lattice structures of the LRE (fcc, dhcp, rhombohedral) and the HRE (hcp) and the variation of the melting points [4, 5] of these elements suggest that because of the larger radial extension of the 4f wavefunctions a hybridization of the 4f electrons with the 5d 6s valence and conduction electrons occurs in the LRE, which is thought to be strong in the beginning and vanishing at the end of the LRE series. NQI measurements in hosts with different 4f-admixtures to the conduction band may help to understand the mechanism by which the 4f electrons affect the EFG at impurity sites. Suitable LRE hosts are La, Ce, Pr, Nd which at room temperature have a dhcp structure in contrast to the simple hcp lattice of the HRE, and Sm with a rhombohedral structure. Eu is cubic and Pm exists only in radioactive form.

In this paper we report a study of the NQI of dilute ^{111}Cd impurities in La, Pr and Nd, which was carried out with the time differential perturbed angular correlation (TDPAC) technique, using the 173–247 keV cascade of ^{111}Cd, populated in the decay of ^{111}In. In Pr the NQI was determined as a function of temperature and pressure, in Nd as a function of temperature and in La only one measurement at 19 K was carried out up to now. In a previous study the room temperature values of the NQI of ^{111}Cd in Pr and Nd had been determined [6].

Experimental Details

For the source preparation carrierfree ^{111}In radioactivity was solute extracted with diethylether from a commercially available hydroacid solution and dropped onto carefully cleaned pieces of the host

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metals (purity 99.9%) which were then electro-gun melted in a vacuum of $5 \cdot 10^{-6}$ Torr on a water cooled copper block. The ^{111}In concentration of the samples was of the order of 1 ppm. In the case of Pr and Nd measurements were carried out with unannealed samples and in samples which had been annealed at 900 K and $5 \cdot 10^{-6}$ Torr for 24 hours, but differences in the corresponding TDPAC spectra were not observed. The La sample was not annealed because oxidation of this highly reactive metal could not be excluded with the available vacuum. The measurements were performed with the 4-detector set-up described in [7]. Hydrostatic pressures up to 7 kbar were produced in an oil cell.

Figure 1 shows the TDPAC spectra $A_2G_{22}(t)$ of ^{111}Cd in Pr at 3 different temperatures. Very similar spectra were observed in Nd. The temperature dependence of the NQI is obviously very strong: At temperatures above 500 K the first maximum of the spin rotation pattern, which at 25 K appears at about 380 nsec, is shifted out of the available time window which in the case of ^{111}Cd is 700 − 800 nsec. This is not the result of any irreversible change of the source: The initial low temperature spectra are fully recovered when the source is cooled down again. The spectrum of ^{111}Cd in La is shown in Figure 2.

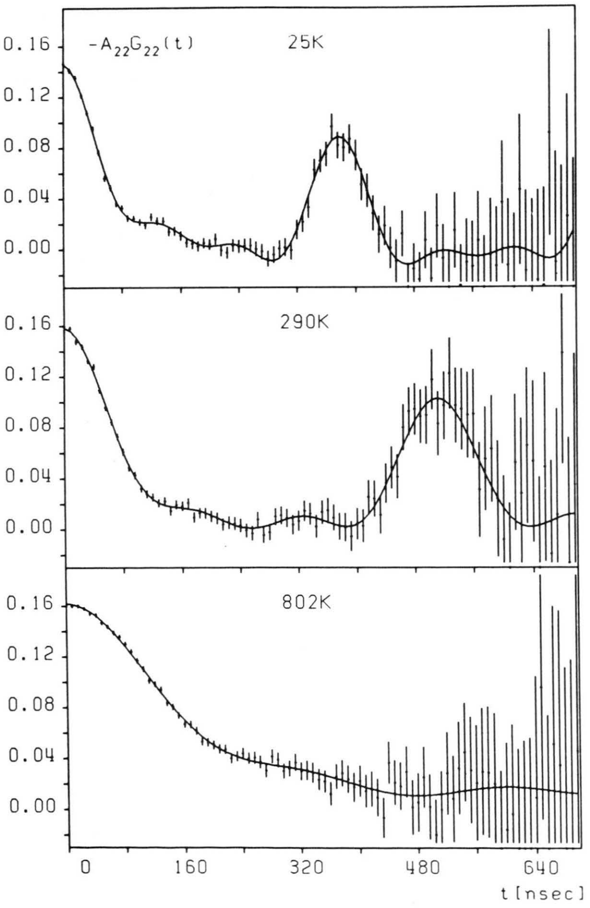

Fig. 1. TDPAC spectra of ^{111}Cd in Pr at different temperatures.

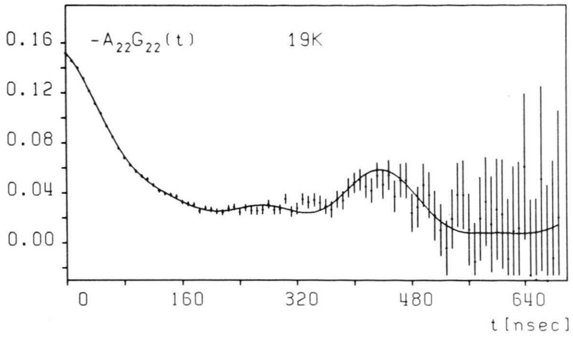

Fig. 2. TDPAC spectrum of ^{111}Cd in La at 19 K.

In all spectra we observe an attenuation of the first maximum of the spin rotation curve. In La only a slight recovery of the anisotropy is found, in Pr and Nd the attenuation is less pronounced. It indicates that not all the nuclear probes experience a unique EFG. The best fits to the spectra were obtained with a 2-fraction model: A fraction f of nuclear probes occupies regular substitutional sites (I) where they experience a unique EFG, while the rest $(1-f)$ on non-regular sites (II) (grain boundaries, imperfections, nearby impurities, ...) is subject to a distribution of interactions. This leads to the expression $\overline{A_2G_{22}(t)} = A_2(f \cdot G_{22}^{\mathrm{I}}(t) + (1-f)\,G_{22}^{\mathrm{II}}(t))$. The theoretical perturbation factor $G_{22}(t)$ for pure quadrupole interactions in polycrystalline samples depends on the quadrupole frequency $\nu_Q = e\,QV_{zz}/h$ and for nuclear spins $I > 3/2$ also on the asymmetry parameter of the EFG $\eta = (V_{xx} - V_{yy})/V_{zz}$ [8]. For impurities on regular sites (I) axial symmetry was assumed because of the symmetry of the dhcp lattice of the hosts. In $G_{22}^{\mathrm{II}}(t)$ which refers to the irregular site (II) a Gaussian distribution of interaction frequencies was admitted. The analysis of the data in terms of this model gave the following results:

(i) **Pr, Nd:** 65(5)% of the impurities are on regular axially symmetric sites. This fraction does not change with temperature. The center frequency $\overline{\nu_Q(\mathrm{II})}$ of the frequency distribution on site II is roughly a factor of 2 smaller than the regular site frequency and has approximately the same temperature dependence. Because of the small value of $\overline{\nu_Q(\mathrm{II})}$ the spectra are not sensitive to the width of the frequency distribution. The regular site frequencies at 290 K are: $\nu_Q(\mathrm{Cd}\,\mathbf{Pr}) = 13.00(10)$ MHz, $\nu_Q(\mathrm{Cd}\,\mathbf{Nd}) = 12.92(20)$ MHz. The errors quoted do not contain the uncertainty of the time calibration. These values are in fair agreement with the result of Mishra et al. [6].

The effect of hydrostatic pressure on the frequency in Pr is small. At 7 kbar and 290 K one has $\nu_Q(\mathrm{Cd}\,\mathbf{Pr};\ 7\ \mathrm{kbar}) = 13.25(11)$ MHz. This corresponds to a temperature coefficient of $(\mathrm{d}\ln\nu_Q/\mathrm{d}P)_{290\,\mathrm{K}} = +2.7(2.3)\cdot 10^{-3}\,\mathrm{kbar}^{-1}$. The pressure coefficient in Nd is presently under investigation.

(ii) **La:** The regular site fraction at 19 K is 20(5)%. The frequency on this site is $\nu_Q(\mathrm{Cd}\,\mathbf{La}) = 14.60(30)$ MHz.

Discussion

From the measured frequencies and the quadrupole moment $Q = +0.83(13)\,b$ [9] of the 5/2 state of ^{111}Cd one obtains for the EFG on regular LRE sites: $V_{zz}(\mathrm{Cd}\,\mathbf{Pr}) = 0.62(2)\cdot 10^{17}\,\mathrm{V/cm^2}$ and $V_{zz}(\mathrm{Cd}\,\mathbf{Nd}) = 0.64(2)\cdot 10^{17}\,\mathrm{V/cm^2}$ at 290 K, and $V_{zz}(\mathrm{Cd}\,\mathbf{La}) = 0.73(2)\cdot 10^{17}\,\mathrm{V/cm^2}$ at 19 K. It is of interest to compare these results with the lattice contribution V_{zz}^{lat} of the EFG. In contrast to the hcp HRE, where one has only one type of regular site, 2 sites of different symmetry exist in the dhcp LRE. The stacking sequence of the dhcp structure is ABACA... where atoms in layers A have hexagonal, those in layers B and C cubic symmetry, which distorts to trigonal if the axial ratio c/a differs from the ideal value.

We have determined the lattice EFG for both sites by a point charge lattice sum calculation. With c and a from [10] and $Z = +3$ for the ion charge, one obtains at 290 K: $V_{zz}^{\mathrm{lat}}(\mathrm{Pr};\mathrm{A}) = 0.88$, $V_{zz}^{\mathrm{lat}}(\mathrm{Pr};\ \mathrm{B},\mathrm{C}) = 0.81$, $V_{zz}^{\mathrm{lat}}(\mathrm{Nd};\ \mathrm{A}) = 0.83$, $V_{zz}^{\mathrm{lat}}(\mathrm{Nd};\mathrm{B},\mathrm{C}) = 0.76$ (all values in units of $10^{15}\,\mathrm{V/cm^2}$). Out result for La agrees with that of [11]. In all cases the difference of V_{zz}^{lat} on the 2 sites is less than 10%. From our present knowledge on impurity EFG's in metals it is justified to assume that the total EFG of an impurity on 2 different sites of the same host scales with the lattice EFG. It is therefore highly improbable that the second ("irregular") site needed to fit our spectra in reality is one of the substitutional LRE sites. From the spectra measured here 2 equally populated sites with a 10% difference in the NQI cannot be distinguished from a single site. We therefore consider the measured values of the EFG as the average of both sites. Under this assumption the electronic enhancement factors are $\alpha = V_{zz}/(1-\gamma_\infty)\,V_{zz}^{\mathrm{lat}} = 2.56(6)$ and 2.68(6) for Pr and Nd, respectively. These values are by a factor of 2 smaller than those predicted by the charge transfer model proposed in [2] to describe the variation of α across the series of the HRE. Some implications of this result have been discussed by Mishra et al. [6].

Both in Pr and Nd the quadrupole frequency ν_Q decreases by about a factor of 3 between 25 K and 900 K. This unusually strong temperature dependence follows neither the $T^{3/2}$-relation of most sp-metals [12] nor the linear relation observed in the HRE [2, 3]: At low temperatures between 25 K and 300 K the decrease is stronger than linear and more pronounced in Pr than in Nd. Above 300 K ν_Q is a linear function of temperature with the same slope in both hosts: $(\mathrm{d}\ln\nu_Q/\mathrm{d}T)_{290\,\mathrm{K}} = -8.4(2)\cdot 10^{-4}\,\mathrm{K}^{-1}$. The relative temperature dependence of V_{zz}^{lat} in Fig. 3, which is the average lattice EFG of the A and the B, C sites calculated with c and a from [10] and normalized to ν_Q at 290 K, shows that only a small part of the decrease of ν_Q is due to the thermal lattice expansion.

The coefficient $(\mathrm{d}\ln\nu_Q/\mathrm{d}T)_{290\,\mathrm{K}}$ of the linear part of ν_Q vs. T of Pr and Nd is compared in Fig. 4 to the corresponding values for ^{111}Cd in Sm [13], Tb [14], Ho [15], and Y [16]. In all these cases one has a linear temperature dependence of the NQI. For ^{111}Cd in Lu $\nu_Q(T)$ has still to be measured. Therefore Y has been inserted in Fig. 4, since it has a comparable valence electron configuration. It is a very interesting observation that the temperature coefficient decreases linearly with the RE atomic number by as much as a factor of 3 between Pr and Y. Only part of this decrease can be attributed to changes of the lattice vibrations across the RE series. In sp-metals the relative decrease of ν_Q is proportional to $(M\Theta_D^2)^{-1}$, which is a measure of the mean square vibration amplitude of the host atoms [12]. In the

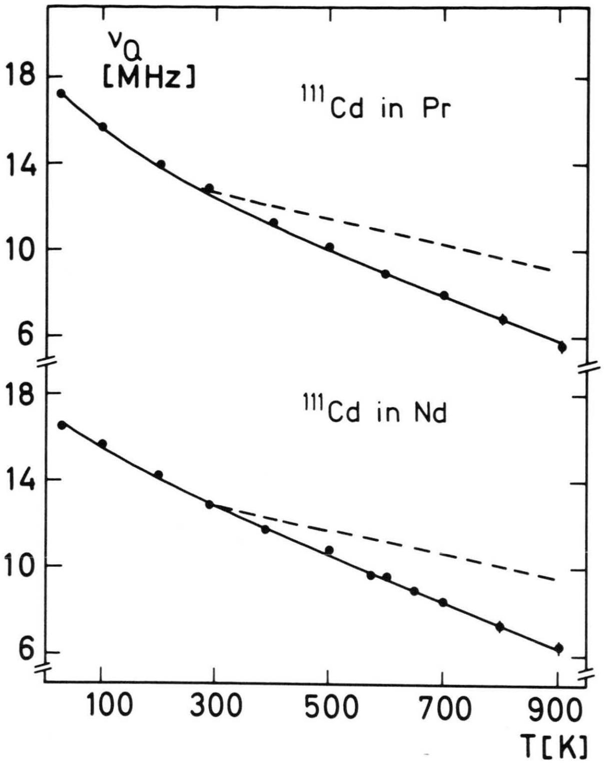

Fig. 3. Temperature dependence of the quadrupole frequency ν_Q of ^{111}Cd in Pr and Nd. The dotted line is the calculated lattice field gradient V_{zz}^{lat}, normalized to the quadrupole frequency at 300 K.

RE $(M\Theta_D^2)^{-1}$ (see dotted line in Fig. 4) decreases by less than a factor of 2 between Pr and Lu.

Another remarkable aspect is that the pressure coefficient $(\mathrm{d}\ln\nu_Q/\mathrm{d}P)_{290\,\mathrm{K}}$ apparently shows a behaviour just opposite to that of the temperature coefficient: In Pr the pressure coefficient is a factor of 3–4 smaller than in the HRE [17].

These temperature and pressure trends may reflect changes in the 4f-electron contribution to the EFG across the RE series. Since the f-sd interaction decreases with increasing number of 4f electrons, the 4f-contribution to the EFG should be most important at the beginning of the LRE series. It is conceivable that the 4f contribution would be rather insensitive to pressure, but due to crystal field effects [3] would react sensitively to changes in temperature. In the LRE then the total EFG would

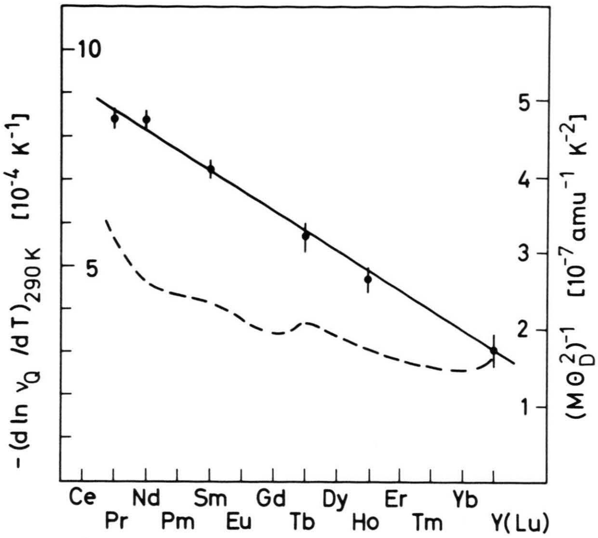

Fig. 4. The temperature coefficient $(\mathrm{d}\ln\nu_Q/\mathrm{d}T)_{290\,\mathrm{K}}$ and the quantity $(M\Theta_D^2)^{-1}$, which is proportional to the mean square vibrational amplitude of the host atoms, as a function of the rare earth atomic number.

have a larger temperature dependence and a weaker pressure dependence than in the HRE. This picture, however, is difficult to reconcile with the observed reduction of the electronic enhancement factor α in the LRE.

For more insight in the importance of the 4f electrons for the impurity EFG in RE hosts, a measurement of the pressure and temperature dependence of the NQI of ^{111}Cd in La, which has an empty 4f shell, would be very helpful. Precise measurements of this kind, however, are difficult – if not impossible – with only 20% of the impurities on regular host sites. We are therefore presently trying to improve the regular site fraction of ^{111}Cd in La by other source preparation techniques, such as e.g. ion implantation.

Acknowledgements

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