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^{111}Cd time-differential perturbed angular correlation study of pressure-induced valence changes in YbAl$_2$

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The quadrupole interaction at ^{111}Cd impurity nuclei in the intermediate-valence compound YbAl$_2$ has been measured under pressure up to 80 kbar by the time-differential perturbed angular correlation spectroscopy. It was found that the quadrupole frequency ν_Q measured on the ^{111}Cd nuclei located at the Al sites in YbAl$_2$ varies nonlinearly and increases by almost four times with the pressure increase up to 80 kbar. A linear correlation between the mean Yb valence, derived from Yb L_3 OFY-XAS and RXES measurements, and the electric field gradient (the quadrupole frequency $\nu_Q = eQV_{zz}/h$) has been observed. The quadrupole frequencies on ^{111}Cd in the GdAl$_2$, YbAl$_3$, TmAl$_3$, and CaAl$_2$ compounds have been also measured. The possibility of determining the valence of Yb in the Yb compounds with p metals from the relation $\nu_Q(\upsilon(P)) = \nu_2 + (\nu_3 - \nu_2)\upsilon(P)$ has been considered.

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INTRODUCTION

Ytterbium intermetallic compounds exhibit interesting physical phenomena such as intermediate valence, Kondo, or heavy fermion behavior.[1] These properties are highly sensitive to chemical environment as well as to external pressure or temperature. This is due to the fact that in the atomic ground state, Yb is divalent with a filled f^{14} shell, but in the solid state, the f electrons may play an active role in the formation of the electronic band structure. The accurate theoretical description of the Yb compounds remains a challenge. Nevertheless, by applying self-interaction corrections[2] in the local-spin-density approximation (LSDA), one could give a valid description of the effective valences of Yb in the Yb compounds. In this description, for a nominal trivalent case, where Yb possesses a localized f^{13} shell, the 14th f electron forms a very narrow band situated among the normal s-d-derived conduction states. The Fermi level is pinned to this narrow band that becomes partially occupied. As a consequence, the total f occupancy is noninteger and falls in between 13 and 14, and the nominally trivalent Yb configuration therefore describes an intermediate valent state with the number of the band f electrons n_f $(0 \leqslant n_f \leqslant 1)$.

The conventional definition of the effective valence for rare earths identifies the valence by the number of the band f electrons having passed into the 5d-electron band (hereinafter, they are referred to as "band f electrons" in inverted commas), $1 - n_f = n_{5d}$, or the number of f holes, $1 - n_f = n_h$.[1] Thus, the Yb valence is determined as $\upsilon = 3 - n_f = 2 + n_{5d} = 2 + n_h$.

In order to obtain quantitative experimental information on the mean valence, researchers widely employ the following techniques: L_{III}-edge x-ray-absorption spectroscopy (XANES),[3] Mössbauer effect (the mean valence derived from isomer shift measurements),[4] and photoemission spectroscopy of the 4f levels.[5]

On the other hand, the electric field gradient (EFG) is a ground-state property of a solid and depends sensitively on the asymmetry of the electronic charge in a crystal. Blaha *et al.*[6] developed a first-principles method to compute the EFGs. They have used the full-potential linear augmented-plane-wave (FP-LAPW) method and have calculated the EFG directly from the self-consistent charge density by solving the Poisson's equation.

However, since the formation of the electron bands by hybridization between the states of different shells leads to a noninteger occupation of the related shells and to the redistribution of the charge density, one can expect that the EFG may also reflect the change of the valence of rare earth ions.

Indeed, the experimental studies of the electric (nuclear) quadrupole interaction (EQI) performed by the time-differential perturbed angular correlation (TDPAC) method in a series of intermetallic compounds RIn$_3$,[7] RSn$_3$,[7] and RAl$_2$ (Ref. 8) ($R = a$ rare earth element) demonstrated a sharp drop of the EFG at ^{111}Cd in YbIn$_3$, in RSn$_3$ with R=Eu and Yb, and in EuAl$_2$ with regard to other trivalent rare earths

R^{+3}. This drop was assigned to be due to the difference in the valence between Eu and Yb with $v=2$ and the compounds with $R=R^{+3}$.

When performing *ab initio* numerical analysis[9] of the experimental data[7] on the EFG of ^{111}Cd in $YbIn_3$, $YbSn_3$, and $EuSn_3$, the authors of Ref. 9 used the FP-LAPW method.[6,10] They showed that the increased V_{zz} value in $R^{+3}In(Sn)_3$ relative to the EFG values observed in $R^{+2}In(Sn)_3$ is caused by an additional polarization of Cd p electrons due to a strong f-p hybridization near the xy plane.[9]

For all $R^{3+}Al_2$ compounds, it was shown[8] that the EQI of ^{111}Cd is characterized by the quadrupole coupling constant (the quadrupole frequency) $\nu_Q \approx 50$ MHz, slightly dependent on Z of a rare earth element, whereas in $Eu^{+2}Al_2$, it is several times lower, $\nu_Q \cong 8$ MHz. No data for $YbAl_2$ were reported in Ref. 8. However, the ^{151}Eu Mössbauer studies[11] under hydrostatic pressure up to 410 kbar revealed that—contrary to expectations—the 4f electrons in $EuAl_2$ remain fully localized, that is, the Eu ions are divalent, even at the reduction of the unit cell volume by ~30%.

On the other hand, the recent results[12] of the pressure-induced valence transition investigations performed by Yb L_3 OFY-XAS and RXES for $YbAl_2$ have revealed that the Yb valence increases from 2.25 at ambient pressure to 2.8 at 80 kbar. Note that the preliminary high-pressure x-ray diffraction studies[13] had found no changes in the crystal structure of $YbAl_2$ up to 80 kbar.

In view of the aforesaid, in this ^{111}Cd-TDPAC study of a pressure-induced valence change, we chose the $YbAl_2$ compound crystallizing in a cubic $MgCu_2$-type structure. The experimental determination of the pressure dependence of the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$ (the quadrupole frequency) measured on ^{111}Cd probed by the TDPAC method enabled us to find a linear dependence of the EFG on the number of the band f electrons, or $1-n_f=n_h=n_{5d}$. We demonstrated that this dependence can be used for determining the valence of Yb ions for the compounds $YbAl_3$ and $YbIn_3$.

EXPERIMENT

The measurements were carried out by the time-differential perturbed angular correlation method using the 171–245 keV γ-ray cascade in ^{111}Cd populated through the 2.8 d isotope ^{111}In electron capture decay. The cascade proceeds via the 245 keV level with the half-life $T_{1/2}=84$ ns, spin $I=5/2$, and quadrupole moment $Q=0.83$ b.

The ^{111}In activity was produced via the ^{109}Ag $(\alpha,2n)$ ^{111}In reaction through irradiating a silver foil with the 32 MeV α beam. The nuclear probe ^{111}In-^{111}Cd was introduced into the lattice of $YbAl_2$, $YbAl_3$, $GdAl_2$, $TmAl_3$, and $CaAl_2$ by the high-pressure synthesis: the constituents (Yb, Tm, Gd, Ca, and Al) taken in proper amounts with an overall weight of about 500 mg were melted together with a small piece of the irradiated silver foil (≈0.5 mg) in a special chamber under a pressure of 80 kbar.[14]

The x-ray diffraction of the powdered samples evidenced that the alloys were single phase; $YbAl_2$ had the cubic Laves-phase structure, while $YbAl_3$ and $TmAl_3$ had the cubic Cu_3Au structure. Our previous experience has proved that this procedure ensures the substitution of ^{111}In for Ru in the Laves-phase compounds $LaRu_2$ and $CeRu_2$,[14] and, as we show below, for Al in $GdAl_2^8$ (Ref. 8) and, presumably, in $YbAl_2$, $YbAl_3$, $CaAl_2$, and $TmAl_3$.

The TDPAC measurements were carried out using a four-detector spectrometer equipped with a small-size hydraulic four-arm press of the capacity up to 300 ton.[15]

As the samples were polycrystalline and paramagnetic at room temperature, the perturbation of the angular correlation can be described by the perturbation factor for the static electric quadrupole interaction:[16]

$$G_{22}(t;\nu_q,\eta,\delta) = s_{20} + \Sigma s_{2n}\cos(\omega_n t) exp(-1/2\,\delta\omega_n t).$$

The hyperfine frequencies ω_n depend on the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$ (the quadrupole frequency) and the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$, where $V_{ii} = \partial^2 V/\partial i^2$ $(i=x,y,z)$ are the principal-axis components of the EFG tensor. The coefficients s_{2n} depend only on η $(1 \geqslant \eta \geqslant 0)$. For the nuclear spin $I=5/2$, $n=1,2,3$. The exponential factor accounts for possible random lattice defects, and δ is the relative half-width of the Lorentzian distribution. Here, we restrict ourselves to the perturbation parameter of the second order since the unperturbed angular correlation coefficient $A_{44} \ll A_{22}$ $(A_{22}=-0.18)$.

The perturbation factor $G_{22}(t)$ describing a nuclear spin precession due to a hyperfine interaction was determined in a usual way from the angular anisotropy, obtained by combining the delayed coincidence spectra measured at the angles of 90° and 180° between detectors, $N(90°,t)$ and $N(180°,t)$, through the expression $R(t) = -A_{22}Q_2G_{22}(t)$, where

$$R(t) = -2[N(180°,t) - N(90°,t)]/[N(180°,t) + 2N(90°,t)],$$

and $Q_2 \approx 0.80$ is the solid-angle correction.

A 100 mg sample of $YbAl_2$ doped with ^{111}In was positioned inside a rocksalt ampoule that was used as a pressure-transmitting medium. The high pressure was generated in a calibrated "toroid-type" device.[17] The calibration of the device was confirmed through measuring the EQI of ^{111}Cd in ^{111}In-doped metallic Zn at normal pressure and at nominal pressure of 30 kbar. The obtained values, $\nu_Q=131$ and 113 MHz, respectively, were in good agreement with those reported by da Jornada and Zawislak.[18]

RESULTS AND DISCUSSION

The ^{111}Cd-TDPAC spectra $R(t) = -A_{22}Q_2G_{22}(t)$ observed in the $YbAl_2$ and $GdAl_2$ compounds at different pressures are presented in Figs. 1 and 2.

The TDPAC spectrum for $YbAl_2$ measured at normal pressure can be best fitted with $\nu_Q=14.0(3)$ MHz assuming the asymmetry parameter $\eta=0$. Here, we note in advance that in all cases, the zero pressure $R(t)$ curves were the same before and after compression, and the values of the quadrupole frequency (QF) ν_Q extracted from the experimental $R(t)$ curves coincided. The EQI parameters measured at normal pressure for $GdAl_2$, $\nu_Q=51(1)$ MHz, $\eta=0$, were in good

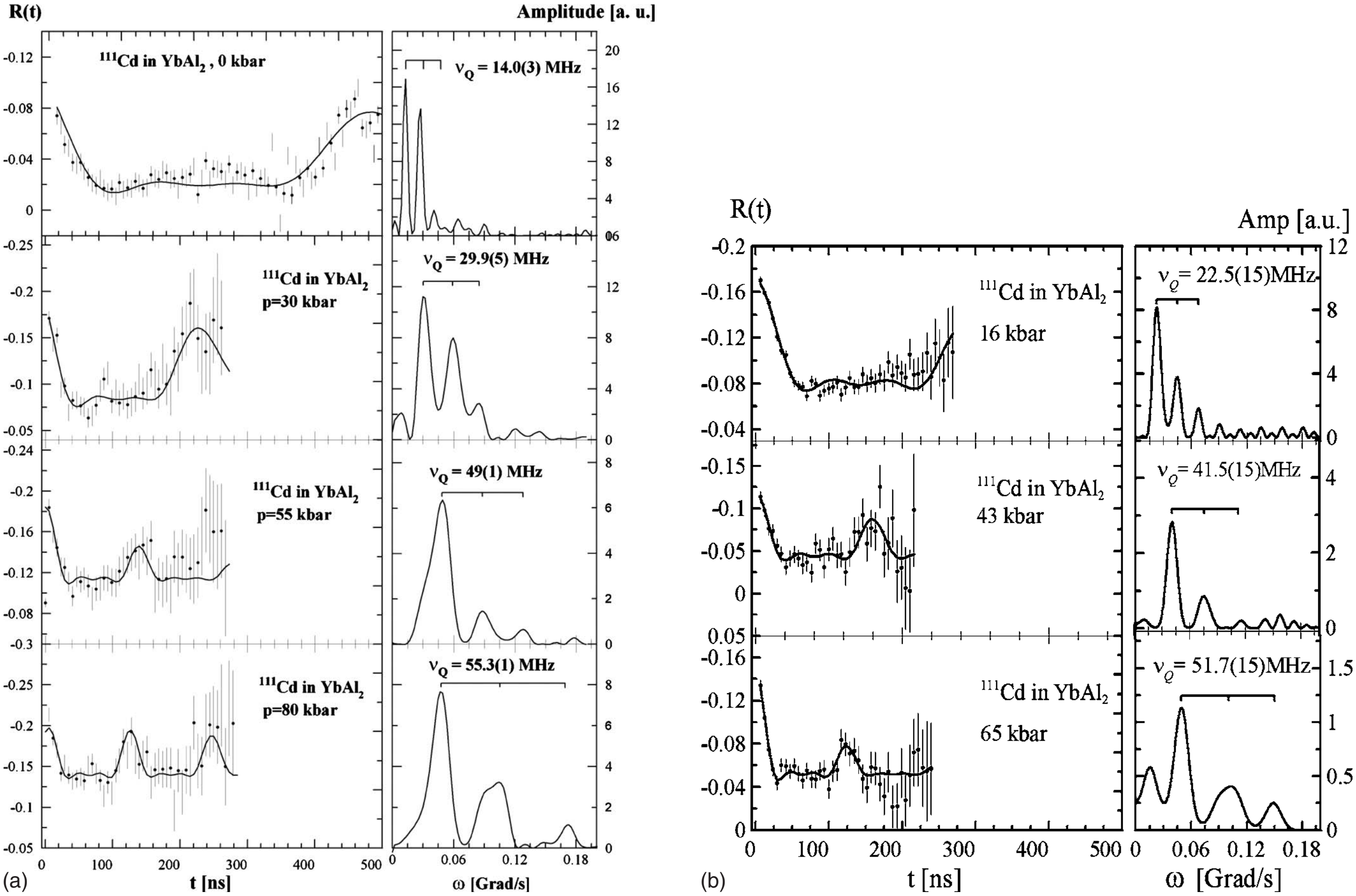

FIG. 1. Time spectra of the angular correlation anisotropy, $R(t)$ (left panel) and their Fourier transforms (right panel), for ^{111}Cd in YbAl$_2$ measured at various pressures. The increase in the deviation of the anisotropy spectrum with the increase of pressure from a zero line is due to the scattering in the sample that varies in shape from a cylinder to a thin disk (see Ref. 19) as pressure rises.

agreement with the data reported in Ref. 8. As was mentioned, this result confirms that in the sample prepared by the synthesis at high pressure with the method described above, ^{111}In substitutes for Al.

The value of the quadrupole frequency ν_Q for YbAl$_2$ is several times lower than that for GdAl$_2$ (where the Gd ion is trivalent); the same was earlier observed for EuAl$_2$.[8]

The variations of the QF, ν_Q, with pressure for ^{111}Cd in YbAl$_2$ and GdAl$_2$ are shown graphically in Fig. 3.

As is seen from the pressure dependence of the quadrupole frequency ν_Q measured on the ^{111}Cd impurity nuclei located at the Al sites in YbAl$_2$ (see Fig. 3), the QF varies nonlinearly and increases by almost four times with an increase in pressure up to 80 kbar. For GdAl$_2$, the QF rises with the same pressure increase by not more than 10%. In Ref. 20, a similar behavior was observed for the pressure-induced change in the isomer shift of EuNi$_2$Ge$_2$, pointing to a valence transition from Eu^{+2} to Eu^{+3} around 50 kbar.

For these particular compounds, this considerable difference in the QF value and its behavior with pressure can be explained as follows. In YbAl$_2$, the ytterbium ion valence at normal pressure is 2.25 and rises to 2.8 (Ref. 12) as pressure increases to 80 kbar. In GdAl$_2$, the gadolinium ion valence is 3, and it does not change as the pressure goes higher in this range. Since the change in valence $[\upsilon=2+n_d=2+(1-n_f)]$ is determined by the filling of the 5d band because of the transfer of f electrons, both the QF value and QF variation with pressure are governed by the fact that the main contribution to the electric field gradient is made by the band f electrons. If the number of the band f electrons remains the same, the increase of the EFG can occur due to the reduction of the lattice parameter, as was shown in Ref. 7 for cubic compounds RIn$_3$. This can explain an inessential pressure-dependent rise of the QF observed for GdAl$_2$.

Using the data obtained in Ref. 12 for the pressure dependence of the ytterbium ion valence, we plotted the dependence of the EFG at ^{111}Cd in YbAl$_2$ on the number of the band f electrons $(1-n_f=n_{5d})$ and found this dependence to be linear (see Fig. 4).

Thus, based on a linear dependence of the EFG (or the quadrupole frequency which is directly measured in the experiment) on the number of the band f electrons $(1-n_f)$, one can determine the valence $[\upsilon=2+(1-n_f)=2+\upsilon(P)]$ of the ytterbium ions from the following relation: $\nu(\upsilon(P))=\nu_2+(\nu_3-\nu_2)\upsilon(P)$, where $\nu(\upsilon(P))$ is the QF measured on ^{111}Cd in an ytterbium compound with a p metal (for example, Al or In), ν_3 is the QF measured in a similar compound containing trivalent ytterbium or a trivalent rare earth, and ν_2 is the QF measured in a similar compound of divalent ytterbium or another divalent metal (for example, Eu or Ca). This relation

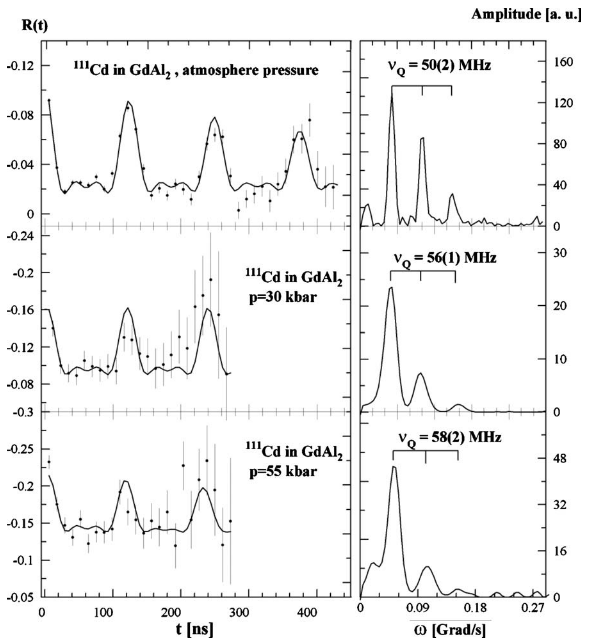

FIG. 2. Time spectra of the angular correlation anisotropy, $R(t)$ (left panel) and their Fourier transforms (right panel), for ^{111}Cd in GdAl$_2$ measured at various pressures.

is similar to the one determining the valence for Eu from isomer shift.[4,21]

Indeed, from the linear dependence of the QF, it was found that for YbAl$_2$, ν_2 is equal to $-5.8(4)$ MHz and the value of $(\nu_3-\nu_2)$ is equal to 76.3(6) MHz. As ytterbium in the compound YbAl$_2$ at normal pressure has a noninteger valence, we measured the QF in CaAl$_2$ for the evaluation of ν_2. This compound has the same crystal structure as YbAl$_2$, but Ca is usually regarded as a divalent analog of Yb. From the ^{111}Cd-TDPAC measurements, we found the value ν_2 for CaAl$_2$ to be equal to 5.7(2) MHz (see Fig. 5) and close to the ν_2 value defined from the QF linear dependence for YbAl$_2$.

It is also known[22] that with the x-ray L_{111} absorption technique, the Yb ion valence in YbAl$_3$ has been found equal to 2.83 at room temperature [i.e., $v(P)=(1-n_f)=0.83$]. To verify our assertion that the $(1-n_f)$-quadrupole frequency dependence is linear for other compounds, we performed the measurements of the QF for the compounds YbAl$_3$ and TmAl$_3$ that have a Cu$_3$Au-type crystal structure. Angular anisotropy spectra for these compounds are given in Fig. 6.

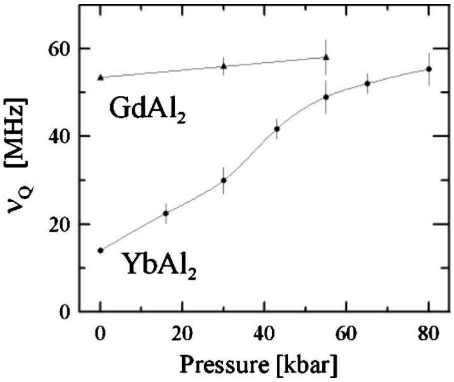

FIG. 3. Pressure dependence of the quadrupole frequency ν_Q for ^{111}Cd in YbAl$_2$ and GdAl$_2$.

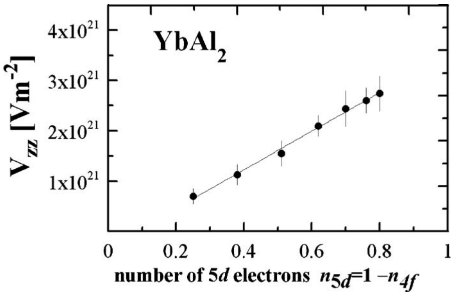

FIG. 4. The electric field gradient $(V_{zz}=\nu_Q h/eQ)$ for ^{111}Cd in YbAl$_2$ versus the number of the band f electrons having passed into the 5d band $(1-n_f=n_{5d})$.

It turned out that for YbAl$_3$, the QF value is equal to 73.3 MHz, and for TmAl$_3$, it is equal to 85.2 MHz. To determine the valence of the Yb ions in YbAl$_3$, we employ the relation suggested above. We assume that the value $(\nu_3-\nu_2)$ does not depend on the crystal structure and remains equal to 76.3 MHz, as it has been found for YbAl$_2$, while the ν_2 value does depend on the crystal structure of the compound. Assuming that $\nu_3(\mathrm{Yb^{+3}Al_3})=\nu(\mathrm{Tm^{+3}Al_3})=85.2$ MHz, we can easily find $\nu_2(\mathrm{Yb^{+2}Al_3})=8.9$ MHz. Then, for YbAl$_3$, the value $v(P)$ is $[\nu(\mathrm{YbAl_3})-\nu_2(\mathrm{Yb^{+2}Al_3})]/(\nu_3-\nu_2)=(73.3-8.9)/76.3=0.84$.

The ratio of these frequencies gives us the value $v(P)=0.84$ and, accordingly, the valence 2.84 for Yb ions in YbAl$_3$. Thus, the valence determined through the TDPAC method is in good agreement with the data[22] on the valence of Yb in YbAl$_3$. If we use this line of reasoning for YbIn$_3$, then, from the data[7] on the quadrupole frequency obtained in ^{111}Cd-TDPAC measurements (for YbIn$_3$, $\nu_Q=38.7$ MHz, and for TmIn$_3$, $\nu_Q=87.7$ MHz), we find that the valence of the Yb ion in YbIn$_3$ is equal to 2.36 and the value of $\nu_2(\mathrm{Yb^{+2}In_3})=11.4$ MHz. This is close but not similar to the value of the Yb ion $(v=2.50)$ obtained in Ref. 23. The difference can be accounted for by the fact that in Ref. 23, the valence has been determined without using the L_{III}-edge x-ray-absorption spectroscopy (XANES) technique.

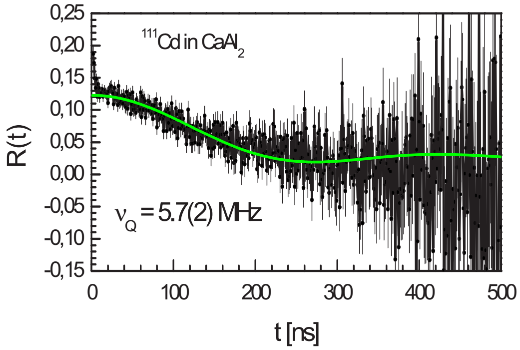

FIG. 5. (Color online) Time spectrum of the angular correlation anisotropy, $R(t)$, for ^{111}Cd in CaAl$_2$, measured at normal pressure.

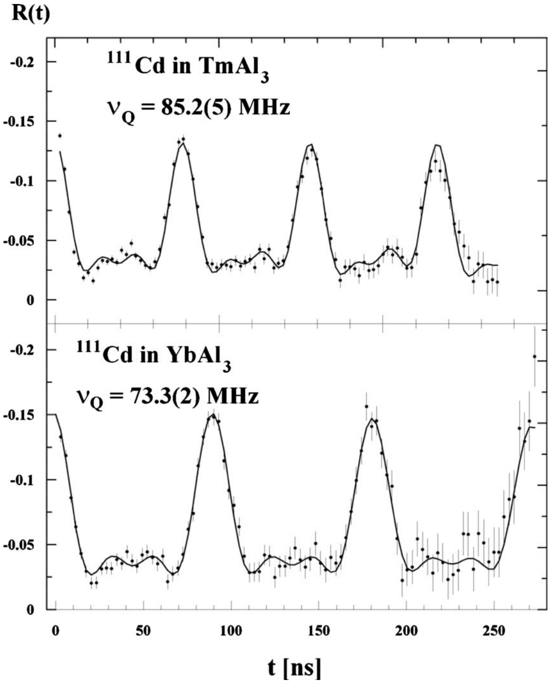

FIG. 6. Time spectrum of the angular correlation anisotropy, $R(t)$, for ^{111}Cd in TmAl$_3$ and YbAl$_3$, measured at normal pressure.

CONCLUSION

To conclude, the results obtained in this work make it possible to state that the variation of the EFG (the quadrupole frequency $\nu_Q=eQV_{zz}/h$) for the Yb compounds with p metals is linearly related to the number of f electrons transferred to the conduction band, i.e., to the number $(1-n_f)$. This regularity allows one to determine the Yb valence by the ^{111}Cd-TDPAC method.

Svane *et al.*,[2] when calculating the Yb ion valence from first principles, have also found a linear correlation between the energy difference of the valent states and the number $(1-n_f)$ of the electrons having come over to the conduction band. However, since the change in the energy difference between two different valent states is caused by a redistribution of f electrons, which, in turn, causes the variation of the EFG, one can speak of an agreement between the theory[2] and the experimental results obtained in the present work. However, for making a correct comparison, theoretical calculations of the relationship between the EFG and the Yb valence are necessary.

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