

The Nuclear Quadrupole Interaction of $^{204\text{m}}\text{Pb}$ in Cadmium Monitored by γ - γ -Perturbed Angular Correlations

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For the first time the nuclear probe $^{204\text{m}}\text{Pb}$ was produced at the on-line isotope separator ISOLDE at CERN and used for time differential perturbed angular correlation experiments. The electric field gradient of $^{204\text{m}}\text{Pb}$ at room temperature in Cd metal was determined to be $V_{zz} = 19(1) \cdot 10^{21} \text{ V/m}^2$. *Ab initio*-calculations of the electric field gradient for the impurities Pt to Bi in cadmium were performed with the full-potential linearized augmented plane waves code WIEN97 to interpret this result. For Au, Hg and Pb, where experimental results are now available, these agree with the calculations within 10 %.

Key words: Nuclear Quadrupole Interaction; Electric Field Gradient; Perturbed Angular Correlation (PAC); *ab-initio* Calculations.

1. Introduction

Electric field gradients (EFGs) in non-cubic metals are widely studied, and also the nuclear quadrupole interaction (NQI) of impurities in metallic host lattices has been investigated extensively (for a compilation of nuclear quadrupole coupling constants in metals see [1]). From the experimental systematics coupled with a tight-binding model a qualitative understanding of the EFGs at sp-impurities in the simple metals Zn and Cd has been developed [2]. Although there are already some studies of Pb as a probe in metals, mainly with the time differential perturbed angular distribution (TDPAD) method, reliable data on the NQI of Pb in zinc or cadmium are still missing.

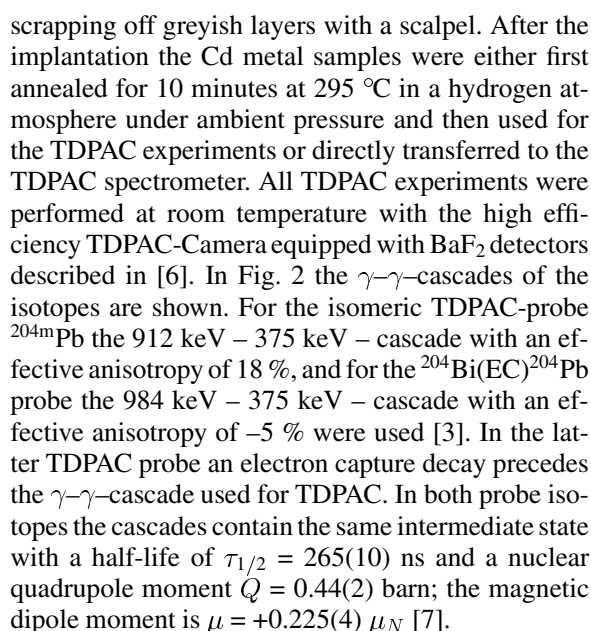
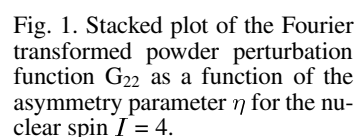
In an early effort the NQIs of the isotope $^{204\text{m}}\text{Pb}$ ($t_{1/2} = 67 \text{ min}$) in various metals as well as in insulating solids were precisely determined by γ - γ

time differential perturbed angular correlation (TD-PAC) measurements using $^{204\text{m}}\text{Pb}$ as produced by a $^{204}\text{Bi}/^{204\text{m}}\text{Pb}$ generator. For Cd, however, only a rough estimate for the nuclear quadrupole coupling constant of $^{204\text{m}}\text{Pb}$ in Cd of $\nu_Q \approx 118 \text{ MHz}$ could be made [3].

Despite of this rather promising early application, the TDPAC probe $^{204\text{m}}\text{Pb}$ was not much used up to now. One reason might be that the nuclear spin I of the intermediate state γ - γ cascade used for TDPAC is $I = 4$ which leads to 7 lines in a Fourier transformed TDPAC time spectrum for axial symmetry and up to 36 lines for non-axial symmetry (see Fig. 1). On the other hand, the long half-life of the intermediate state of 265 ns provides an excellent frequency resolution.

2. Experimental Methods and Results

We have used the on-line isotope separator ISOLDE / CERN [4] to implant $^{204\text{m}}\text{Pb}$ or ^{204}Bi with



an energy of 60 keV into pieces of Cd metal. The production of such beams requires the newly installed laser ion source at ISOLDE [5] which allows the production of ion beams almost free of isobaric contamination. The surfaces of the Cd metal pieces directed towards the beam were carefully cleaned by

Due to the limited energy resolution of the BaF₂ detectors ($\Delta E/E \approx 13\%$) the same energy adjustment of the spectrometer was used for both cascades. At the energies of the described γ - γ TDPAC cascades of ^{204m}Pb a time resolution of approximately 600 ps FWHM (Full Width Half Maximum) was achieved. We used a time per channel of ≈ 1 ns, which allowed to monitor the time dependence of the anisotropy over

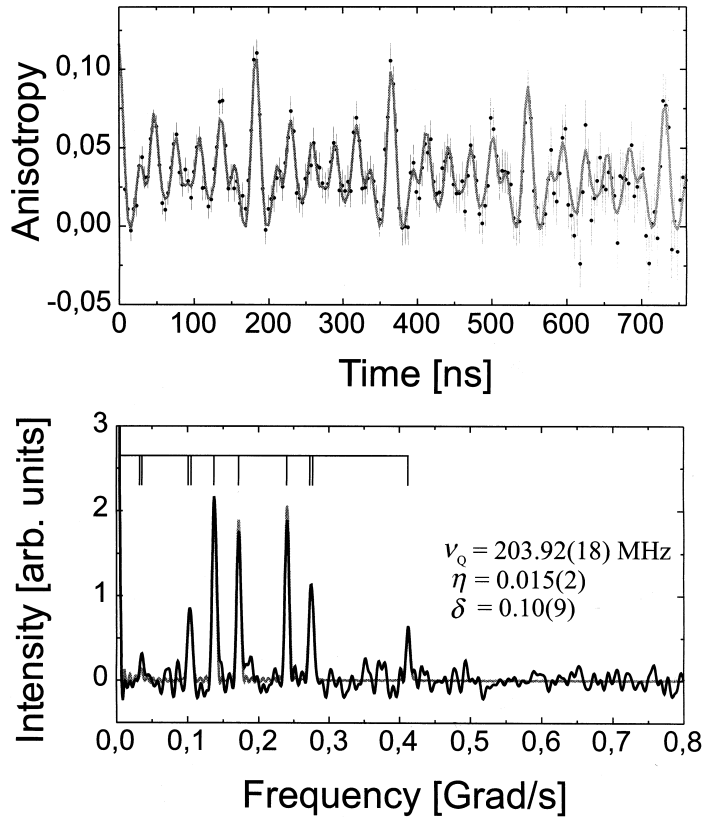


Fig. 3. The TDPAC time spectrum (top) and its Fourier transform (bottom) of $^{204\text{m}}\text{Pb}$ in Cd metal. The grey lines show the least-squares-fitting for the NQI parameters: $\nu_Q = 203.92(18)$ MHz, $\eta = 0.015(2)$, effective anisotropy 11.2(6) %, Lorentzian line broadening 0.10(9) %. The frequency bar in the Fourier spectrum indicates the nuclear precession frequencies.

a time range of ≈ 760 ns, i. e., approximately 3 times the half-life of the intermediate state. The frequency resolution was about ≈ 9 Mrad/s (Kaiser-Bessel data window, weighting factor 6).

A detailed description of the TDPAC method and data analysis is given in [8].

In Fig. 3 the TDPAC time spectrum and its Fourier transform of $^{204\text{m}}\text{Pb}$ implanted in Cd metal is shown. For data presentation the spectrum was compressed from 800 to 200 channels. This spectrum was obtained after the annealing procedure described above. A total of $14 \cdot 10^6$ coincidences were recorded for this spectrum. An analysis of the original time spectrum by a least-squares-fitting routine yields the following NQI parameters: nuclear quadrupole coupling constant $\nu_Q = 203.92(18)$ MHz, asymmetry parameter $\eta = 0.015(2)$, effective anisotropy 11.2(6) % and Lorentzian line broadening $\delta = 0.10(9)$ %. This NQI corresponds to an EFG tensor with $V_{zz} = 19(1) \cdot 10^{21}$ V/m². Since the hexagonal lattice of cadmium metal should result in an EFG with axial symmetry, the non-zero asymmetry parameter as well as the small line broadening must be due to lattice imperfec-

tions. We obtained no characteristic $^{204\text{m}}\text{Pb}$ -TDPAC spectra without an annealing prior to the TDPAC measurements.

With the $^{204}\text{Bi}(\text{EC})^{204}\text{Pb}$ probe in Cd metal, the TDPAC spectra showed no characteristic NQI signal at all. Here, the annealing procedure had no significant influence on the NQI signal.

2.1. Ab-initio Electric Field Gradient Calculations

In order to interpret the result of the present experiment, ab-initio calculations of the EFG for the impurities Pt to Bi in cadmium were performed with the full-potential linearized augmented plane waves (FLAPW) code WIEN97 [9]. This theoretical method had been demonstrated earlier to give very reliable results for the EFG for many different concentrated systems [10]. The isolated impurity case was simulated by a supercell of 36 atoms with the lattice structure of Cd constructed around the impurities. All calculations were carried out at the experimentally known lattice parameters. The calculations were performed with the most modern density functional using

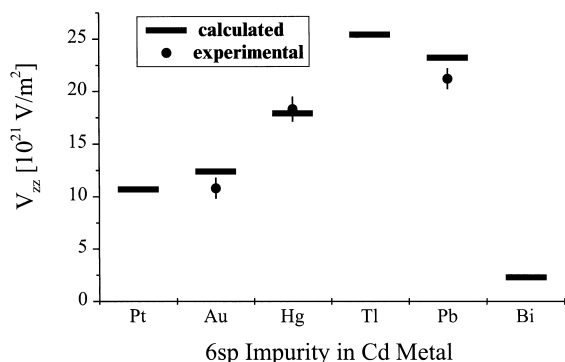


Fig. 4. Comparison of the calculated and experimentally determined EFG values for the 6sp impurities Pt to Bi in cadmium metal (experimentally determined EFGs are extrapolated to 0 K, for Au and Hg in Cd see [1]).

generalized gradient corrections [11]. For the final calculations, 30 k-points in the irreducible wedge of the Brillouin zone were employed. Calculations with only 10 k-points and also with smaller supercells of 16 and 18 atoms had demonstrated that the results as presented in Fig. 4 can be considered with reasonable confidence. In order to compare the calculated EFG values with those experimentally determined the experimental EFG values [1] in Fig. 4 are extrapolated to 0 K according to the temperature dependence of the EFG for Cd in cadmium metal [12].

The fact that for Au [13], Hg [14, 15] and Pb, where experimental results are now available, the measured values of the EFG agree with the calculations within 10 % also testifies for the reliability of the present approach. With the use of the small supercells of 16 and 18 atoms a very similar behavior for the 5sp-series Pd to Xe in Cd had been obtained earlier [16]. Here the values are typically a factor of 2 smaller than for the 6sp impurities, as expected from the simple tight-binding model used earlier in the qualitative interpretation of the experimentally observed trends [2].

3. Discussion and Conclusion

Three isomeric PAC isotopes are now available at the on-line isotope separator ISOLDE at CERN: $^{111\text{m}}\text{Cd}$ ($t_{1/2} = 49$ min), $^{199\text{m}}\text{Hg}$ ($t_{1/2} = 43$ min) and $^{204\text{m}}\text{Pb}$ ($t_{1/2} = 67$ min). With the “new ISOLDE TD-PAC isotope” $^{204\text{m}}\text{Pb}$ the EFG of the impurity Pb residing on a lattice site in Cd was determined to be: $V_{zz} = 19(1) \cdot 10^{21} \text{ V/m}^2$, $\eta = 0.015(2)$.

Ab initio-EFG calculations agree within approximately 10 % with this experimental value. This excellent agreement was achieved even without taking lattice relaxation about the impurities into account. Since these calculations could be extended to a series of 5sp and 6sp impurities in Cd, the reliability of FLAPW supercell calculations to describe the EFG for impurities in metals was corroborated.

The non-zero asymmetry parameter of the $^{204\text{m}}\text{Pb}$ -EFG, as well as the small but existing line broadening are due to lattice imperfections and reflect the great sensitivity of this isotope to deviations from axial symmetry. This is a consequence of the fact that the intermediate state of this isotope has an integer nuclear spin I and therefore the eigenvalues of the nuclear quadrupole Hamiltonian operator depend linearly on η , whereas in the case of half-integer spins this dependence is quadratic, e.g., for $^{111\text{m}}\text{Cd}$ and $^{199\text{m}}\text{Hg}$ both with $I = 5/2$. A further advantage of the $^{204\text{m}}\text{Pb}$ probe compared to $^{111\text{m}}\text{Cd}$ ($\tau_{1/2} = 85.0(7)$ ns) and $^{199\text{m}}\text{Hg}$ ($\tau_{1/2} = 2.45(2)$ ns) [6] is the long half-life of its intermediate state which should allow to achieve an excellent frequency resolution of 3 Mrad/s. Therefore, this isotope should be well suited to study concentrations and coordination geometries of defects in solids. In life sciences an application of the $^{204\text{m}}\text{Pb}$ probe would be the investigation of the coordination and the dynamics of the Pb binding site in new catalytic DNA molecules which can be used as metal sensitive bio sensors [17]. A more detailed understanding of the interaction of transition metal ions with these biomolecules is essential to optimize their efficiency and selectivity as metal sensors – a quite beneficial role for the toxic triple of TDPAC probes $^{111\text{m}}\text{Cd}$, $^{199\text{m}}\text{Hg}$ and $^{204\text{m}}\text{Pb}$.

The fact that there are no characteristic NQI frequencies with the $^{204}\text{Bi}(\text{EC})^{204}\text{Pb}$ probe in cadmium metal is yet not completely understood and has to be further investigated. An explanation might be that in the decay of ^{204}Bi also the isomeric state $^{204\text{m}}\text{Pb}$ is populated. Since the anisotropies of the cascades of $^{204}\text{Bi}(\text{EC})^{204}\text{Pb}$ and $^{204\text{m}}\text{Pb}$ have opposite signs, a compensation of the signals might occur by even small admixtures of the $^{204\text{m}}\text{Pb}$ -cascade which has a significantly higher anisotropy.

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