Nuclear quadrupole and hexadecapole interactions in crystals of lutetium compounds

G. K. Semin and A. M. Raevskiĭ

A. N. Nesmeyanov Institute of Organoelemental Compounds, Academy of Sciences of the USSR

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The first experimental proof of the existence of nuclear hexadecapole interactions has been obtained, in the particular case of crystals of lutetium compounds.

Although nuclear hexadecapole interactions were predicted by Casimir[1] in 1936, attempts to experimentally observe these interactions, dating back to[2] 1955, continue down to the present day. However, no unambiguous experimental proof of the existence of nuclear hexadecapole interactions has yet been obtained.

The Hamiltonian for this problem is

$$H = H_Q + H_M \tag{1}$$

where the Hamiltonian H_Q describes nuclear quadrupole interactions, and the Hamiltonian H_M describes the nuclear hexadecapole interactions.

A joint solution of the secular equations in the axial approximation for the nuclear hexadecapole interactions yields the following values of the frequencies for a nuclear spin $I = 7/2$:

$$\nu_{QM(1/2-3/2)} = \frac{\Delta E_{(1/2-3/2)}(\eta)}{28} e^2 Qq_{zz} - \frac{12}{448} e^2 Mm,$$

$$\nu_{QM(3/2-5/2)} = \frac{\Delta E_{(3/2-5/2)}(\eta)}{28} e^2 Qq_{zz} - \frac{10}{448} e^2 Mm, \tag{2}$$

$$\nu_{QM(5/2-7/2)} = \frac{\Delta E_{(5/2-7/2)}(\eta)}{28} e^2 Qq_{zz} + \frac{20}{448} e^2 Mm.$$

Here $\nu_{QM(ij)} = \nu_{Q(ij)} + \nu_{M(ij)}$ are the observed frequencies in the spectrum of the nuclear quadrupole resonance; $\Delta E_{(ij)}(\eta)$ are the differences between the roots of the secular equation for the purely quadrupole interaction (see Ref. 2; the specific solution of the secular equation for a spin $I = 7/2$ in the radicals is given in Ref. 12.); $\eta = |(q_{xx} - q_{yy})/q_{zz}|$ is the asymmetry parameter of the tensor representing the gradient of the electric field; $eq_{xx} = \partial^2 V/\partial x^2$, $eq_{yy} = \partial^2 V/\partial y^2$, and $eq_{zz} = \partial^2 V/\partial z^2$ ($|q_{yy}| < |q_{xx}| < |q_{zz}|$) are the principal components of the tensor representing the gradient of the electric field; $e^2 Qq_{zz}$ is the constant of the nuclear quadrupole interaction (eQ is the nuclear quadrupole moment); and $e^2 Mm$ is the constant of the nuclear hexadecapole interaction (eM is the nuclear electric hexadecapole moment, and $em = \partial^4 V/\partial z^4$ is the maximum principal component of the tensor of fourth derivatives of the potential V at the position of the nucleus).[2]

It follows from symmetry considerations that the nuclear quadrupole interaction should be dominated by the valence p-electrons of the resonant atom, while the nuclear hexadecapole interaction should be dominated by the valence d- or f-electrons.[3,4]

On the basis of general considerations, we would expect the largest hexadecapole moment for nuclei with the charge distributions distorted to the greatest extent. We would intuitively expect a hexadecapole distortion of this sort for nuclei with a maximum quadrupole moment.

The requirements listed above are satisfied best by the lutetium atom. For ^{175}Lu (nuclear spin $I = 7/2$), for example, the nuclear quadrupole moment is larger than for any other nuclei with half-integer spin ($eQ = 5.68$ b). The valence shall of the lutetium atom is represented by d-electrons. Furthermore, in the case of a perturbation of the electrons of the f-shell of the lutetium atom by coordination interactions, there can be an additional (and extremely important) contribution to the nuclear hexadeca-

TABLE I. Spectral parameters of the nuclear quadrupole resonance and of the nuclear hexadecapole interaction of ^{175}Lu at 77 K.

Compound	Position of lutetium atom	Transition frequencies, MHz			e^2Qq_{zz}	η	e^2Mm,	$\frac{e^2Mm}{e^2Qq_{zz}}$, %
		1/2 – 3/2	3/2 – 5/2	5/2 – 7/2	MHz		MHz	
Lu_2O_3	I	156.57 ± 0.06	312.81 ± 0.03	469.29 ± 0.16	2190.0 ± 0.4	0.015 ± 0.003	0.3 ± 2.0	0.01 ± 0.09
	II	158.85 ± 0.07	159.07 ± 0.06	251.34 ± 0.06	1217.2 ± 0.2	0.5840 ± 0.0004	– 3.8 ∓ 1.1	– 0.3 ∓ 0.1
$Lu(CH_3COO)_3 \cdot 4H_2O$	I	95.400 ± 0.025	77.856 ± 0.015	119.933 ± 0.025	598.5 ± 0.1	0.780 ± 0.001	0.4 ± 0.4	0.07 ± 0.07
$Lu_3Fe_5O_{12}$	I	37.0 ± 0.4	70.0 ± 0.8	111.0 ± 0.8	505.1 ± 3.1	0.14 ± 0.01	66.6 ± 13.2	13.2 ± 2.6
$Lu(NO_3)_3$ $4H_2O$	I	56.07 ± 0.05	84.35 ± 0.05	99.84 ± 0.05	546.5 ± 0.2	0.234 ± 0.001	– 372.6 ∓ 0.8	– 68.2 ∓ 0.2
	II	53.63 ± 0.05	83.99 ± 0.05	94.52 ± 0.05	531.0 ± 0.2	0.184 ± 0.001	– 422.8 ∓ 0.8	– 79.6 ∓ 0.2

pole interaction, since the changes in the nuclear hexadecapole interaction are inversely proportional to the fifth power of the distance.

Our measurements, our analysis, and our check of data in the literature[5,6] have shown that for crystals of lutetium compounds not all the nuclear quadrupole resonance spectra of ^{175}Lu can be described by a secular equation without a hexadecapole correction. The results of the studies and of calculations from (2) are shown in Table I. It follows from this table that the nuclear hexadecapole interactions can vary over a broad range, from a level statistically indistinguishable from zero to a level comparable in magnitude to the nuclear quadrupole interactions.

In summary, these results provide the first experimental confirmation of the existence of a nuclear hexadecapole interaction.

The nuclear quadrupole resonance spectra of ^{175}Lu were studied at 77 K with the help of an ISSh-2-13 pulsed nuclear-quadrupole-resonance spectrometer, manufactured by the Special Design Bureau of the Institute of Radio Engineering and Electronics, Academy of Sciences of the USSR.[7] For measurements of the frequencies and widths of the nuclear-quadrupole-resonance lines, we used methods involving a transfer of a heterodyne spectrum,[7] zero beats,[8] and frequency markers.[9] All of the methods that were used yielded similar results in repeated measurements. We found it possible to determine the reproducibility of the experimental results, which turns out to be about $0.1\Delta\nu_{1/2}$ (where $\Delta\nu_{1/2}$ is the width of the spectral line at half-maximum). The magnitude of the reproducibility is given in Table I and was used in solving system of equations (2) by the standard least-squares procedure with respect to e^2Qq_{zz}, e^2Mm and η (Ref. 10). All the calculations were carried out on an Iskra-226 microcomputer.[11]

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