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ON THE COMPENSATION OF A NONUNIFORM CHEMICAL (MONOPOLE) SHIFT OF THE MÖSSBAUER LINE

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Abstract. — The proportionality between the small variations of total S-electron density and spin density at the site of nucleus location permits proposing a method of compensating by a properly chosen radio-frequency field the most essential source of Mössbauer line broadening: the non-uniform chemical (monopole) shift. The proposed method for narrowing of the Mössbauer lines can be used for precise determination of certain HFS parameters and for starting the operation of a γ-laser (gaser). It is also important for the extension of Mössbauer spectroscopy to all problems, which need much narrower lines (probably, up to the minimum width of solid state NMR line, i.e. ca $10^{-15}$ eV).

In real crystals the chemical (monopole) shift (1) of (HFS) nuclear levels, proportional to the total density of electrons on this nucleus [1], varies from nucleus to nucleus. For long-lived isomers this results in broadening of the Mössbauer line that exceeds then the natural line width by many orders of magnitude [2]. This is the most essential impediment to use of long-lived isomers in gamma-resonance (Mössbauer) spectroscopy and for producing of γ-lasers (gasers) [2, 3, 4], since it seemed that such a broadening cannot be suppressed by radio-frequency methods [4, 5], the monopole shift being the same for all HFS components.

A method is proposed for compensating the variation in the monopole shift of a Mössbauer line by that of HF splitting of an opposite direction and the same value. The HF splitting variation may be for instance due to a change in the Fermi contact interaction that is proportional to the electron spin density on the nucleus [6]. Such a compensation is possible in a properly chosen periodical homogeneous magnetic field.

The choice of a crystal compound for which small variations in the total electron density on the nucleus are proportional to these in the spin density is assumed to be possible.

The alternating magnetic field is applied in order to attain a compensating value for the coefficient of proportionality between variations in the monopole shift and HF splitting.

It will be noted that HFS in the alternating field is determined for the quasi-energy of the nucleus [7, 8].

The most simple theoretical case would be that, when the spin of the ground state is zero, and the static homogeneous magnetic field $H$ circumscribes a cone with top angle $2 \theta$ around axis $Z$ with a frequency $\omega$. Making use of the Majorana theorem [9] and of the solution for a Majorana pseudo-particle [9, 10] with spin $1/2$, the HFS for the nucleus quasi-energy $A$ with spin $I$, magnetic moment $\mu$, and monopole shift $\delta \hbar$ will be

$$A_m = I \omega + m \Omega + \delta$$

$$\Omega = \sqrt{\omega^2 + 4 \omega_M^2 + 4 \mu H \hbar \cos \theta}$$

where $m = -I, -I + 1, ..., I$ are the eigenvalues of spin projection onto the direction of the rotating field, $\omega_M = \mu H/(2 \hbar)$ is the Larmor precession frequency of the Mayorana pseudo-particle in field $H$. 

(1) The chemical shift in Mössbauer spectra is called the isomer or monopole shift to distinguish it from the chemical shift in NMR, which has somewhat different nature.
Field $H$ is the sum of the external field $H_e$ and the effective field $H_f$ due to Fermi interaction, i.e.

$$H = H_e + H_f$$

where $\mu_e$ is the electron magnetic moment, $T$ is the temperature, $K$ is the Boltzmann factor. When (4) is fulfilled, the effective field $H_f$ continuously follows the direction of $H_e$ without essential fluctuations [10]. It will be taken into account that

$$\delta = <\delta> + \Delta \delta; \quad H_t = <H_t> + \Delta H_t$$

where parentheses $<A>$ stand for a certain value $A$ averaged over all nuclei, and $\Delta A$ defines the deviation of $A$ from $<A>$. It follows from the assumption of proportionality between small variations in electron and spin densities (2) on passing from nucleus to nucleus that

$$h \Delta \delta = \kappa \mu \Delta H_t$$

where $\kappa$ is a dimensionless constant that can be of the order $0.01$-$0.1$ [11, 12, 13].

Dropping the small values of order $|\Delta H_t/H|^2$ in (2) we obtain

$$\Delta A_m = A_m - <A_m> = \Delta \delta + \frac{\mu}{h} \frac{\Delta H_t}{h} C_m$$

where the value $C_m$ standing for the compensation coefficient of the $m$th HFS component is

$$C_m = \frac{2 <\omega_m> + \omega \cos \theta}{<\Omega>}$$

With proper selection of values $\omega, \theta, H_e$ the $m$th component of the quasi-energy HFS can become zero. This would require fulfilment of the compensation condition

$$C_m = - \kappa.$$  

When $\omega = -2 <\omega_m>$, eq. (9) reduces to

$$\frac{m}{T} \sin \frac{\theta}{2} = - \kappa.$$

Then the condition for compensation of monopole broadening will be

$$H_e > T \times 10^6 \text{ Oe/grad}; \quad \kappa \ll 1; \quad \omega = -2 <\omega_m>; \quad H_{\perp} = 2 \kappa H_e \frac{I}{m}.$$

(2) Note, that we are dealing here with the proportionality between small variations of isomer shift $\delta$ and local magnetic field at the nucleus $H_e$ (e. g. due to the change of the volume of elementary cell caused by various imperfections of the crystal — see [2]) rather than with the (non-existent) proportionality between above-mentioned magnitudes themselves

$$(\delta \propto |\psi(0)|^2 + |\psi(0)|^2$$

and $H_{\perp} \propto |\psi(0)|^2 - |\psi(0)|^2$. $H_{\perp}$ is the amplitude of the alternating (rotating) part of the field (3). For instance, at $T = 0.1 \text{ K}; \quad \kappa = 0.01$; $I = 2; \quad |m| = I; \quad \mu H = 3 \times 10^{-7} \text{ eV}$, we must have $\omega/2 \pi \approx 40 \text{ MHz}, H_e > 10^4 \text{ Oe}, H_{\perp} > 20 \text{ Oe}.$

The compensation method could be used as a certain spectroscopic means for determination of HFS characteristics such as $\kappa = h \Delta \delta/\mu \Delta H_t$ and $\mu(H_e + H_f)$. Indeed, let product $m \sin \theta/2$ be the same for all compensating angles $\theta_m$ at a constant frequency $\omega$. Then $|\kappa|$ and $\mu(H_e + H_f)$ can be readily obtained from (10), as the latter will be valid only provided $\omega = -2 <\omega_m>$. As to application of the method to gasers, fast applying of the compensating radio-frequency field, with other critical conditions fulfilled, is equivalent to the opening action of a shutter in common lasers.

The method can be used for a more common form as well. Then the field $H = H_e + H_f = (H_e + H_f)$ will change both in direction $n$, as in the above case, and in the value of $H_e + H_f$. Using the method of Hamiltonian reduction over the $s$-matrix, in the same way as this was done by one of the authors [5], the field $H$ and the compensation coefficient can be expressed in a parametric form

$$|H| = \frac{2hI}{|\mu|} \left\{ \left[ \lambda^2 + \lambda \phi + \frac{1}{4} (\phi^2 + \phi^2 + \gamma^2) \right] + \frac{1}{2} (\phi + 2 \lambda) \cos \gamma \right\}^{1/2};$$

where $H_e = \frac{h}{\mu} \left[ \gamma \cos \psi + (\phi + 2 \lambda) \sin \gamma \sin \psi \right];$ $H_f = \frac{h}{\mu} \left[ -\gamma \sin \psi + (\phi + 2 \lambda) \sin \gamma \cos \psi \right];$ $H_{\perp} = -\frac{h}{\mu} \left[ \psi + (\phi + 2 \lambda) \cos \gamma \right].$

Then the compensation condition retains its form (9). Here $\omega/2 \pi$ is the fundamental frequency of the compensating radio-frequency signal; $\psi(t) = \tilde{\psi}(t) + \omega_p t; \quad \gamma(t) = \tilde{\gamma}(t) + \omega_r t,$ where $p, q, r$ are arbitrary integers; $\tilde{\psi}(t), \tilde{\phi}(t), \tilde{\gamma}(t)$ are arbitrary periodical functions of period $T$; $\lambda$ is an arbitrary real constant over the range $-\frac{\pi}{T} \leq \lambda \leq \frac{\pi}{T}$. (3) Note the difference in signs of $\omega$ and $<\omega_m>$. The field must rotate in a direction opposite to nuclear precession.
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\[ \phi, \psi, \gamma \] are the first time derivatives:

\[ \dot{\phi} = \frac{d\phi}{dt}, \quad \dot{\psi} = \frac{d\psi}{dt}, \quad \dot{\gamma} = \frac{d\gamma}{dt}. \]

In principle, the three arbitrary functions and on free constant \( \lambda \) make possible not only the fulfilment of the condition for compensation of monopole broadening (9), but also suppression by radio-frequency methods [4, 5] of the magnetic and electric quadrupole variations in the monopole shift.

The idea of compensation by means of a controlled radio-frequency field can be extended to a more complex case, when both isomer states have non-zero spins, and the HFS represents a superposition of the monopole shift and of the magnetic and quadrupole HF interactions (HFI).

As in the model case, this would require a crystalline compound for which variations in local HFI on passing from nucleus to nucleus would be proportional to those in the monopole shift. Then, similarly to the above, proper selection of the radio-frequency field would make possible a situation such that the fluctuations of the total magnetic-quadrupole HFI and those of the monopole shift for one of the HFS components would appear to be mutually compensated (4). Moreover other HFS variations not proportional to those of the monopole shift can also be compensated by using a more complex compensating fields.

(4) Not only the constant variations can be compensated, but also the fluctuations in the monopole shift slowly changing with time (in terms of the radio-frequency signal period).

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The modern literature on gasers (gamma-lasers) and directly related problems

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