Cancellation of inhomogeneous chemical shift of Mössbauer line

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The proportionality of the total *S*-electron density at the location of the nucleus, in the case of a Fermi contact interaction, makes it possible to propose the use of a specially selected radio-frequency field to cancel out the most significant cause of Mössbauer-line broadening of long-lived isomers, namely, the inhomogeneous chemical (monopole) shift.

One of the most dangerous mechanisms causing broadening of Mössbauer lines of long-lived isomers in real crystals is the inhomogeneous chemical (monopole) shift, which is caused by variations (due to defects, dislocations, and others) of the total electron density at the excited nuclei.[1] These broadenings cannot be suppressed by radial-frequency methods,[2,3] since the monopole shift is the same for all the hfs components.

In principle, however, it is possible to choose compounds such that the hfs variation due to the change in the spin electron density at the excited nucleus turns out to be proportional to the changes of the total electron density at the same nucleus, at least for small density variations. Since radio-frequency methods[2,3] make it possible to control to some degree the proportionality coefficient between the magnitude of the hfs of the m-th component and the change of the electron spin density C_m, there exists in principle a possibility of choosing C_m such that the inhomogeneous chemical shift is cancelled out by an equal and opposite variation of the hfs.

By way of illustration of the realizability of this idea, let us consider the case when the mechanism connecting the variation of the hfs with the variation of the electron spin density is a Fermi contact interaction.[4] The alternating field H acting on the nucleus consists of an external field H_e and an effective field H_ρ due to the Fermi interaction.

The alternating magnetic field is applied to enable the coefficient of proportionality between the variations of the monopole shift and the hyperfine splitting to reach the compensating value.

It is important to note that in an alternating field the hfs is defined for the quasienergy of the nucleus (see[3]).

The theoretically simplest case is when the spin of the ground state is equal to zero, and the homogeneous magnetic field H, which is constant in magnitude, describes a cone with an apex angle 2θ about the z axis, with frequency ω.

Applying the Majorana theorem[5] and using the solution of the problem for a Majorana quasiparticle[5,6] with spin 1/2, we can easily obtain the hfs for the quasienergy Λ of the nucleus with spin I, magnetic moment μ, and monopole shift $\hbar\delta$:

$$\Lambda_m = I\omega + m\Omega + \delta\,, \tag{1}$$

$$\Omega = \sqrt{\omega^2 + 4\omega_M^2 + 4\omega\omega_M\cos\theta}\,, \tag{2}$$

where $m = -I,;\ -I+1, \ldots,\ I$ are the eigenvalues of the projection of the spin I on the direction of the rotating field, and $\omega_M = \mu H/2I\hbar$ is the Larmor recession frequency of the Majorana pseudoparticle in the field.

With this, we have

$$H = H_e + H_\rho, \tag{3}$$

if

$$\left|\frac{H_e\mu_0}{kT}\right| \ll 1; \qquad \left|\frac{H_e\mu_0}{\hbar\omega}\right| \gg 1, \tag{4}$$

where μ_0 is the magnetic moment of the electron, T is the temperature, and k is the Boltzmann factor. When conditions (3) are satisfied, the effective field H_ρ assumes continuously the direction of the field H_e without significant fluctuations.[6]

We recognize that

$$\delta = \langle\delta\rangle + \Delta\delta; \qquad H_\rho = \langle H_\rho\rangle + \Delta H_\rho, \tag{5}$$

where the angle brackets of $\langle A\rangle$ denotes averaging of a certain quantity A over all the nuclei, and the symbol ΔA denotes the deviation of A from $\langle A\rangle$. From the assumption that small variations of the electron density are proportional to the spin density on going from nucleus to nucleus, it follows that

$$\hbar\,\Delta\delta = \kappa\mu\Delta H_\rho, \tag{6}$$

where κ is a dimensionless constant, the order of magnitude of which is 0.01–0.1 according to the experimental data.[7,8] Discarding in (2) small quantities of order $|\Delta H_\rho/H|^2$, we find

$$\Delta\Lambda_m = \Lambda_m - \langle\Lambda_m\rangle = \Delta\delta + \frac{\mu\Delta H_\rho}{\hbar}\,C_m, \tag{7}$$

where C_m, which we call the cancellation coefficient for the m-th component of the hfs, is

$$C_m = \frac{2\langle\omega_M\rangle + \omega\cos\theta}{\langle\Omega\rangle}\,\frac{m}{I}\,. \tag{8}$$

Choosing the quantities ω, θ, and H_e we can cause the m-th hfs component of the quasienergy to vanish. To this end it is necessary to satisfy the cancellation condition

$$C_m = -\kappa\,. \tag{9}$$

At $\omega = -2\langle\omega_M\rangle$, Eq. (9) assumes the particularly simple form

$$\frac{m}{I}\sin\frac{\theta}{2} = -\kappa\,. \tag{10}$$

The idea of cancellation with the aid of an adjustable-radio-frequency field makes it possible to generalize the considered model to the more complicated case when both states of the isomer have nonzero spins, and the hfs is a simultaneous superposition of a monopole shift and of magnetic and quadrupole hyperfine interactions (hfi).

Just as in the model case, it is necessary to have a crystalline compound in which the variations of a local hfi on going from nucleus to nucleus are proportional to the variations of the monopole shift. Then, in analogy with the method shown in the present paper, a suitable choice of the radio-frequency field makes it possible to cause the fluctuations of the summary magnetic-quadrupole hfi to cancel the fluctuations of the monopole shift for one of the hfs components.1) In addition, it is possible, by making the compensating field more complicated, to suppress other variations of the hfs, which are not proportional to the variations of the monopole shift.

1)It is possible to cancel out not only constant variations, but also fluctuations of the monopole shift which vary slowly in time (relative to the period of the radio-frequency signal).

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Erratum: Cancellation of inhomogeneous chemical shift of Mössbauer line [JETP Lett. 19, 324 (1974)]

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On p. 324 the abstract should read:

"The proportionality between the small variations of the total *S*-electron density and spin density at the location of the nucleus, in the case of Fermi contact interaction, makes it possible to propose the use of a specially-selected radio-frequency field to cancel out the most significant cause of Mössbauer-line broadening of long-lived isomers, namely the inhomogeneous chemical (monopole) shift."