Theory of Mössbauer spectra in an electric field

A. S. Ivanov, A. V. Kolpakov, and R. N. Kuz'min

Moscow State University

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The influence of an electric field on the shape of the resonance γ-ray absorption spectrum in ferroelectrics is discussed. Relations describing the spectrum in the case of magnetic-dipole transitions between states with total angular momenta 1/2 and 3/2 are presented. A formula is obtained which makes it possible to determine the number of domains reoriented through 90° from the experimental data. Estimates are given which prove that the Mössbauer effect can be used to study the domain structure of polycrystalline ferroelectrics.

The influence of an electric field on the shape of the γ-ray resonance absorption spectrum in substances possessing piezoelectric properties was studied by Bloembergen [1,2]. In the present paper, we study the Mossbauer spectrum of polycrystalline ferroelectrics, taking into account the 90°-reorientations of the domains [3-5] in polarization and aging processes.

The experimental investigations of the Mossbauer spectra of ferroelectics [6] have exhibited the presence of a considerable electric field gradient at the nuclei, sufficient to split the resonance absorption line. This electric field gradient, which arises as a result of tetragonal distortions of the lattice, is axially symmetric, and its symmetry axis is parallel to the vector **P** of the spontaneous polarization of the domain. The switching on of an external electric field **E** leads to a rearrangement of the domain structure, and 90°-reorientations occur, i.e., the vectors of the spontaneous polarization of the domains, and with them the axes of the electric field gradient, change their direction by 90°, aligning themselves closer to the field direction. Since the intensity $I_{fi}(\chi)$ of the components of the absorption spectrum depends on the angle χ between the direction $\mathbf{n}_\gamma$ of incidence of the γ-rays and the axis of quantization, we should expect changes in the shape of the spectrum when the directions of polarization of the domains change by an angle $\pi/2$. We note that a 180°-repolarization does not affect the Mossbauer spectrum, since the probability of absorption of a photon is invariant with respect to inversion.

We shall assume that a polycrystalline sample of unit volume, consisting of N domains, is in an unpolarized state before the external field is switched on. Then the axes of the electric field gradient are statistically distributed uniformly over all directions, and the absorption spectrum is a series of peaks equal in magnitude. The Gol'danskiĭ-Karyagin effect is not taken into account [7]. In an external field, the shape of the spectrum is determined by the formula

$$I_{fi}=\frac{\alpha}{4\pi}\int I_{fi}(\chi)F(\theta)\,d\Omega, \tag{1}$$

where the indices i and f characterize the initial and final states of the nucleus, α is the density of Mossbauer nuclei $NF(\theta)d\Omega/4\pi$ is the number of domains whose polarization vectors lie in the solid angle $d\Omega=\sin\theta\,d\theta\,d\varphi$; θ and φ are the spherical-polar angles of the vector $\mathbf{n}\equiv\mathbf{P}/P$ in the coordinate frame with the z axis directed along the external field. Expanding the distribution function $F(\theta)$ in spherical harmonics and using the representation of $I_{fi}(\chi)$ in the form of an expansion in Legendre polynomials, it is easy to obtain a general formula describing the spectrum.

From the point of view of practical use, the case of magnetic dipole transitions between states of the nucleus with total angular momenta 1/2 and 3/2 is the most interesting. In this case the spectrum is a doublet, and the intensities of its components are determined by the relations

$$I_\sigma=\tfrac{1}{2}(I_0-\delta),\quad I_\pi=\tfrac{1}{2}(I_0+\delta),$$
$$\delta\equiv 0{,}1I_0F_2Y_{20}(\theta_\gamma),\qquad F_2\equiv\int F(\theta)\,Y_{20}(\theta)\,d\Omega, \tag{2}$$

where I_0 is the total intensity of the absorption peaks and θ_γ is the angle between the vectors $\mathbf{n}_\gamma$ and **E**. The indices π and σ correspond to transitions with and without change of the angular-momentum component. As can be seen from formula (2), there occurs a decrease of one of the peaks and an equivalent increase of the other. The experimentally measurable difference δ between the intensities of the components is directly related to the coefficient F_2 in the expansion of the distribution function in spherical harmonics.

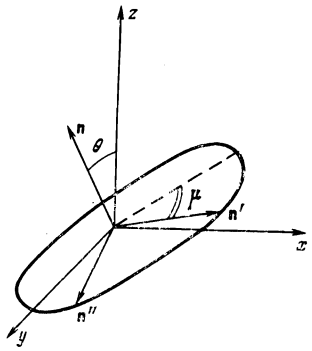
We shall estimate the magnitude of the change in the spectrum, starting from a model of noninteracting domains. The energy of a domain in the electric field is $\epsilon=-(\mathbf{E}\cdot\mathbf{P})V$, where V is the volume of the domain. Since in our case there are six polarization directions, each domain can be found in six energy states. We shall assume that, after the external field has been switched on, there is time for thermodynamic equilibrium to be established in the system of domains before the recording of the Mossbauer spectrum is begun. In this case, the distribution of domains over the energy states will be a Boltzmann distribution. We shall separate out into a subsystem all the domains whose possible polarization directions are characterized by the six vectors $\pm\mathbf{n}$, $\pm\mathbf{n}'$ and $\pm\mathbf{n}''$. The number of domains in the state with energy ϵ_1 in this subsystem is

$$3N\pi^{-2}Z^{-1}\exp\{-\epsilon_1/kT\}, \tag{3}$$

where Z is the partition function and T is the temperature.

The total number of domains having energy ϵ_1 is obtained by summing the expression (3) over all subsystems possessing the common vector **n** and arbitrary possible vectors $\mathbf{n}'$ and $\mathbf{n}''$. Let μ be the angle between the vector $\mathbf{n}'$ and the projection of the z axis on to a plane orthogonal to the vector **n** (see the figure). Summation of the expression (3) over all subsystems satisfying the conditions mentioned above reduces to integration over μ between the limits 0 and $\pi/2$. Correspondingly, the number of domains whose polarization vectors lie in the solid angle $d\Omega$ is equal to

$$\frac{N}{4\pi}F_\lambda(\theta)\,d\Omega=\frac{3N}{\pi^2}e^{\lambda\cos\theta}\int_0^{\pi/2}Z^{-1}\,d\mu\,d\Omega,$$
$$\lambda\equiv EPV/kT. \tag{4}$$



The vectors n, n′ and n″ in the coordinate frame with the z axis directed along the external field.

Starting from formula (4), it is not difficult to show that in the state of maximum polarization, i.e., for $\lambda \to \infty$, the quantity $F_2 = 2(15/\pi)^{1/2}$, and the maximum possible number of 90°-reorientations is equal to $m_{max} \approx 0.6N$. We shall determine the number m of 90°-reorientations, using the fact that the number of domains in which the symmetry axes of the electric field gradient are collinear can vary only as a result of rotations through an angle $\pi/2$:

$$m = N \sum_{l=2}^{\infty} F_l \int_0^{\theta^*} Y_{l0}(\theta) \sin\theta \, d\theta, \qquad (5)$$

where l are even and θ^* satisfies the equation $F(\theta^*) + F(\pi - \theta^*) = 2$.

Calculating the contribution to m_{max} from the term containing F_2 in the right-hand side of formula (5), we convince ourselves that it is approximately equal to 0.53N and differs insignificantly from the exact value of m_{max}. This indicates the comparatively small contribution to m from terms in the sum with $l > 2$, even in the limiting case of maximum polarization of the sample, and enables us to obtain a simple formula for estimating the number of 90°-reorientations. Discarding the terms with $l > 2$ in (5), we find

$$m \approx {}^1/_6 (5/3\pi)^{1/2} N F_2. \qquad (6)$$

In experiments of Fedchenko et al.[5], it was found that in fields $\sim 3 \times 10^4$ V·cm^{-1} the number of 90°-reorientations equals ~0.3N. Determining the corresponding value of F_2 from the relation (6), we obtain, using (2), $\delta = 0.181 I_0$.

The estimate given above shows that the change in the shape of the spectrum is sufficient for experimental detection and for obtaining information on the domain structure of ceramics.

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