HYPERFINE STRUCTURE OF BRAGG MAXIMA IN MÖSSBAUEROGRAPHY

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HYPERFINE STRUCTURE OF BRAGG MAXIMA IN MÖSSBAUEROGRAPHY

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A remarkable feature of the Mössbauer effect is that the energy width of the nuclear gamma-resonance line is comparable with the magnitude of the splitting of nuclear levels in intracrystalline fields. Therefore, in resonance absorption spectra the hyperfine structure (h.f.s.) of the lines is resolved. From the distance between the components one can determine the magnitude H_{eff} of the magnetic field at the nucleus or the magnitude of the electric-field gradient (e.f.g.), when the nuclear moments μ_{nucl} and Q are known, and also in some cases determine the angle between H_{eff} and the axis of the axially symmetric e.f.g. tensor. The h.f.s. of resonance spectra may be rather complicated, for example if a superposition appears of several h.f.s.' s corresponding to nuclei with different atomic surroundings. The shape of the h.f.s. is also affected by the anisotropy of the Lamb–Mössbauer factor (^{1}), the asymmetry of quadrupole splitting (^{2,3}), and relaxation processes (^{4,5}). The ratios between transition intensities depend on the angle between the direction of absorption and the direction of H_{eff}; for the $3/2 \to 1/2$ transition of a completely split "magnetic spectrum" with 6 components, their intensities are in the ratio $3:0:1:1:0:3$ along the magnetic axis and $3:4:1$ in the perpendicular direction. For a polycrystalline or multidomain sample, averaging the angular dependences of the components gives the ratio $3:2:1$. Studies of the angular dependence of h.f.s. components are usually carried out on plates of single crystals cut in certain directions.

From a study of the diffraction of resonance gamma quanta one can obtain not only all the information indicated above, but also extract fundamentally new data concerning the atomic and magnetic structure of crystals. The possibilities of Mössbauerography in determining scattering phases have been considered in works ($^{6-8}$). Bragg maxima may have a hyperfine structure; here it is evident that the energy spectrum of the diffraction peak is exactly the same as in the case of absorption, since it is determined by the splitting of the ground and excited levels of the nucleus in the effective fields and by the selection rules. The ratio between the intensities of the individual components of the spectrum, however, proves in the case of scattering to be more contrasted and more sensitive to the direction of the field. As an example, one may cite how the intensity ratio of the 6 components of the magnetic spectrum in the Bragg maximum for Fe^{57} changes depending on the direction of H_{eff} in a single-domain crystal. If the scattering angle $2\theta \sim 90°$, then when the angle of H_{eff} with the normal to the reflecting plane χ changes from 90 to 0°, the ratio between the intensities changes respectively from $9 : 16 : 1 : 1 : 16 : 9$ to $9 : 2 : 1 : 1 : 2 : 9$, $\varphi = 90°$, and with a change of the angle φ (see Fig. 1) for fixed $\chi = 45°$ it becomes equal to $9 : 0 : 1 : 1 : 0 : 9$ for $\varphi = 0°$ and $9 : 5.8 : 1 : 1 : 5.8 : 1$ for $\varphi = 90°$. For small scattering angles the ratio almost does not change with an azimuthal change in the direction of H_{eff}, but depends strongly on the angle of H_{eff} with the normal to the reflecting plane. The study of the energy spectrum of one reflec-

···does not give complete information on the direction of $\mathbf{H}_{\text{eff}}$, but an analysis of the spectra for 2–3 reflections can completely determine the orientation of $\mathbf{H}_{\text{eff}}$ (a means μ_{at}) relative to the reflecting plane (with an accuracy up to $\pm$). It is noteworthy that the ratio of the spectral intensities is not affected by $f'(\vartheta)$– the probability of the Mössbauer effect (and other factors connected with the scattering geometry, the shape of the specimen, etc.).

If the angular resolution of the detector does not make it possible to separate individual Bragg maxima, especially at large scattering angles, then the ratio of the intensities of the components turns out to be different; for example, in the case when $\mathbf{H}_{\text{eff}} \perp \mathbf{k}_1, \mathbf{k}_2$ ($\chi = 90°$, $\varphi = 90°$), for all scattering angles the ratio becomes $1.8 : 4 : 1$ instead of $9 : 16 : 1$ for the Bragg maximum.

In studying diffraction from a single crystal containing only nuclei with one value of the field $\mathbf{H}_{\text{eff}}$, the study of the h.f.s. in a Bragg reflection gives no new information about the direction of the intracrystalline fields relative to the reflecting plane in comparison with registration with a broad beam.

Fig. 1

In the case of a polycrystal, the h.f.s. of the spectrum recorded with a broad beam is the result of averaging the h.f.s. over arbitrary directions of $\mathbf{H}_{\text{eff}}$, which gives the ratio $3 : 2 : 1$, varying only weakly with the change of scattering angle. With collimation of the beam and isolation of the Bragg reflection in scattering from a polycrystal, we again obtain complete information on the direction of $\mathbf{H}_{\text{eff}}$ in the crystal, since each reflection receives a contribution from microcrystallites (assumed to be single-domain) having a definite orientation of the crystallographic axes, which also determines the angle of $\mathbf{H}_{\text{eff}}$ with the normal to the reflecting plane.

χ	90°	45	0°
$2\theta = 10°$	$9 : 2.5 : 1$	$9 : 9.2 : 1$	$9 : 15.5 : 1$
$2\theta = 40°$	$9 : 4.1 : 1$	$9 : 5.2 : 1$	$9 : 10 : 1$

Unfortunately, in the case of a polycrystal it is necessary to take into account the influence of the anisotropy of the probability of the Mössbauer effect $f(\theta)$

and $f'(\theta)$.

Analogous arguments are applicable to the case of quadrupole interaction for determining the e.f.g., as well as the asymmetry parameter η. Of greater interest is the case when the crystal contains nuclei with different $\mathbf{H}_{\text{eff}}$ in magnitude and direction. However, if the splitting of the levels of all resonant nuclei in the unit cell differs substantially, so that the overlap of the resonance energies is insignificant, then each component of the spectrum will manifest itself in the diffraction peak independently of the others, and the ratio between the intensities is determined by the relative directions of "its own" fields. In this case, from the h.f.s. one can obtain information on the magnitude and direction of two or more fields, as before.

In the case of overlapping resonances of different nuclei, the study of the h.f.s. of the Bragg peak must be begun with the construction of the structure amplitude, since now the h.f.s. will not be, in contrast to the case of absorption and incoherent scattering, a simple superposition of elementary h.f.s. The intensity of resonant scattering in the direction of a diffraction maximum will correspond to the addition of the amplitudes f_{Mj}, and not of the intensities, with the corresponding geometrical factor. The f_{Mj} may be elliptically polarized in the case of the presence of a magnetic field.

Then

$$F_{hkl} = \sum_j f_{M_j}(\mathbf{k}_1 \mathbf{H}_{j\text{eff}},\ \mathbf{k}_2,\ E_j)\, e^{2\pi i(hx_j+ky_j+lz_j)}$$

(for simplicity, the contribution of Rayleigh scattering to F_{hkl} is not considered), and the ratio between the intensities of the components in the h.f.s. of the diffraction peak can provide information on the spatial distribution of differently oriented fields. The dependence of f_{M_j} on the magnitude and direction of the field may lead to the appearance of magnetic maxima whose h.f.s. is not distorted by interference with Rayleigh scattering.

Table 1

Compound	Space group	T_N, °K	Magnetic reflections hkl	2θ	Rayleigh reflections hkl	2θ
FeO	O_h^6—$Fm3m$	198	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$	9°58′	1 1 1	20°
FeO	O_h^6—$Fm3m$	198	1 0 0	11°24′	2 0 0	23°46′
FeO	O_h^6—$Fm3m$	198	1 1 0	16°18′		
FeO	O_h^6—$Fm3m$	198	$\frac{3}{2}\ \frac{1}{2}\ \frac{1}{2}$	19°6′		
α-Fe_2O_3	D_{3d}^6—$R\bar{3}c$	250	1 1 1	10°50′	1 1 0	13°24′

Compound	Space group	T_N, °K	Magnetic reflections hkl	2θ	Rayleigh reflections hkl	2θ
α-Fe_2O_3	D_{3d}^6—$R\bar{3}c$	675	1 0 0	11°50′	2 0 0	24°
FeSn	D_{6h}^1—$p6/mmm$	373	0 0 $\frac{1}{2}$	5°16′	100 + 001	10°40′
FeSn	D_{6h}^1—$p6/mmm$	373	1 0 $\frac{1}{2}$	12°4′	1 0 1	14°50′
FeSn	D_{6h}^1—$p6/mmm$	373	0 0 $\frac{3}{2}$	16°6′	1 1 0	18°18′
FeSn	D_{6h}^1—$p6/mmm$	373	1 1 $\frac{1}{2}$	18°58′	200 + 111	20°58′
FeSn	D_{6h}^1—$p6/mmm$	373			0 0 2	21°26′
FeGe	D_{6h}^1—$p6/mmm$	411	0 0 $\frac{1}{2}$	6°	1 0 0	11°58′
FeGe	D_{6h}^1—$p6/mmm$	411	1 0 $\frac{1}{2}$	12°54′	0 0 1	12°10′
FeGe	D_{6h}^1—$p6/mmm$	411	1 1 $\frac{1}{2}$	20°44′	1 0 1	16°40′
FeGe	D_{6h}^1—$p6/mmm$	411	1 0 $\frac{3}{2}$	21°38′	1 1 0	21°48′
$FeCO_3$	D_{3d}^6—$R\bar{3}c$	35	1 1 1	9°38′	1 1 0	14°4′
$FeCO_3$	D_{3d}^6—$R\bar{3}c$	35	1 0 0	12°30′		
$ErFeO_3$	D_{3d}^6—$R\bar{3}c$	620	0 1 1	11°2′	0 0 2	13°6′
$ErFeO_3$	D_{3d}^6—$R\bar{3}c$	43	1 0 1	11°30′		

Note. The angles were calculated for the wavelength of the Mössbauer transition of Fe^{57}, equal to 0.86 Å, with an accuracy of up to 6′.

Let us give possible nuclear reflections in which there is no contribution from Rayleigh scattering for some antiferromagnets (Table 1). The appearance of these reflections is connected with the magnetic ordering of atoms. The ratio between the intensities of the magnetic components in antiferromagnetic superstructure reflections, irrespective of the field direction, turns out to be $9:0:1:1:0:9$.

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