Crystal-Structure Investigations with the Mössbauer Effect

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Theoretical and experimental work on investigation of the diffraction of resonant γ rays by crystals is reviewed.

Nuclear physics has given rise to more than one method for the investigation of crystal structure; it is enough to recall neutron diffraction, which now occupies an incontestable place among diffraction methods of investigation.

The discovery by Mössbauer (1958, 1959) of the optimum conditions for resonant absorption or scattering of γ rays gave crystallographers a new instrument of investigation by means of which it became possible to undertake new types of investigation for example of phase transitions, kinetic transformations, and determination of crystal-structure characteristics.

In the spectroscopic scheme the Mössbauer effect, or nuclear gamma resonance (NGR) as it is sometimes called, is, in its range of application, very close to radiospectroscopic methods: nuclear magnetic resonance, NCR, electron spin resonance and their variants. Numerous investigations in the field of NGR have been summed up in a series of monographs (Frauenfelder, 1962; Goldanskij, 1963; Wertheim, 1964).

In contrast to the above mentioned spectroscopic methods, the Mössbauer effect has made it possible to carry out investigations on scattering and diffraction which considerably enlarge the scope of NGR.

Let us consider the process of formation of a diffraction maximum in the scattering of γ rays by a crystal containing resonant scattering nuclei. It is quite clear that scattering will take place in two channels; one part scatters on nuclei of the resonant scattering isotope, the second part scatters on all the atoms of the crystal. Each diffraction maximum will therefore contain a resonant nuclear component as well as Rayleigh-electron components. The quantitative relations of each of the components will depend on the effective cross sections of the electronic and nuclear scattering, and on the absorption coefficient and concentration (p) of the resonant scattering nuclei.

As it is possible to obtain enriched samples it is always possible to allow for the presence of the incoherent background which is caused by some disorder in the arrangement of Mössbauer atoms at lattice sites.

In addition, the dependence of the scattering amplitude on the concentration of Mössbauer isotopes makes it possible to define the scattering phases.

Formally, the structural scattering amplitude of monochromatic γ rays with wavelength λ_0 on a crystal containing at the same time not only ordinary but also Mössbauer atoms (of one type only) can be presented as:

$$F(H) = \sum_{j=1}^{N} f_j \exp 2\pi i \delta_j = (f_{R_N} + p f_N) \sum_{i=1}^{n} \exp 2\pi i \delta_i$$
$$+ \sum_{j=n+1}^{N} f_R \exp 2\pi i \delta_j, \quad (1)$$

where f_{R_N}, f_{R_j} are the form factors of the Rayleigh scattering of a Mössbauer atom and the jth atom, f_N is the nuclear scattering factor, n is the number of sites occupied by Mössbauer atoms in the unit cell,

$$H = h, k, l \text{ and } \delta_j = \left(\frac{\Delta S}{\lambda_0 r_j} \right).$$

The first term of this equation is the structural scattering amplitude for the Mössbauer atoms, the second is that of the other atoms of the unit cell. As an illustration let us take a parallel comparison of the isomorphous method and Mössbauer diffraction on samples containing different resonant-scattering nuclei. The structural amplitudes of an identical reflexion for two isomorphous compounds are as follows:

$$F_{\mathrm{I}}(H) = f_{\mathrm{I}} \exp 2\pi i \delta_1 + \sum_{j=2}^{N} f_j \exp 2\pi i \delta_j$$

$$F_{\mathrm{II}}(H) = f_{\mathrm{II}} \exp 2\pi i \delta_1 + \sum_{j=2}^{N} f_j \exp 2\pi i \delta_j.$$

Then the difference $F_{\mathrm{II}}(H) - F_{\mathrm{I}}(H) = (f_{\mathrm{II}} - f_{\mathrm{I}}) \exp 2\pi i \delta_1$ is the ground for defining the phase of a ray scattered in this direction by the replaced atom in the unit cell.

By analogy with isomorphism, for Mössbauer diffraction on the samples with different concentrations of the resonant-scattering nuclei we shall have the following equations for the amplitudes of identical reflexions:

$$F_{\mathrm{I}}(H) = (f_{R_N} + p_1 f_N) \sum_{i=1}^{n} \exp 2\pi i \delta_i + \sum_{j=n+1}^{N} f_{R_j} \exp 2\pi i \delta_j$$

$$F_{\mathrm{II}}(H) = (f_{R_N} + p_2 f_N) \sum_{i=1}^{n} \exp 2\pi i \delta_i + \sum_{j=n+1}^{N} f_{R_j} \exp 2\pi i \delta_j,$$

from which

$$F_{11}(H) - F_1(H) = (p_2 - p_1) \sum_{i=1}^{N} f_N \exp 2\pi i \delta_i$$

(non-centrosymmetric crystal)

$$F_{11}(H) - F_1(H) = (p_2 - p_1) \sum_{i=1}^{N} f_N \cos 2\pi \delta_i$$

(centrosymmetric crystal) .

In this case there is a possibility of obtaining values for the phase of the spectrum by the use of vector diagrams in the complex plane. The formalism of this procedure has been considered by Kuz'min, Kolpakov & Zhdanov (1966).

Of course, it is easier to prepare samples with different isotropic composition than it is to obtain the isomorphous compounds.

Nowhere above have we emphasized the fact that the nuclear scattering amplitude depends on the frequency of the incident radiation. If the source is given a motion relative to the scattering crystal, there will be a Doppler shift of frequency of the incident radiation and its energy will no longer coincide with that of the resonant γ transition in the nuclei of the scatterer. By means of the Mössbauer effect it is possible to distinguish between the contributions to the intensity of the Bragg maximum from the nuclear and electronic scattering and so obtain additional information about the crystal structure.

As both processes of scattering are coherent the scattering intensity in the direction of a Bragg maximum equals

$$I(H,S) = [f_{R_N} + p f_N(S)]^2 \left(\sum_{i=1}^{n} \exp 2\pi i \delta_i \right)^2$$
$$+ \left(\sum_{j=n+1}^{N} f_{R_j} \exp 2\pi i \delta_j \right)^2$$
$$+ 2[f_{R_N} + p f_N(S)] \sum_{i=1}^{n} \sum_{j=n+1}^{N} f_{R_j} \cos \delta_{ij} . \quad (2)$$

Here S is the energy shift.

Separating in (2) the nuclear and electronic components of the scattering and the term which is dependent on the interference of both kinds of scattering we have:

$$I(H,S) = I_R + I_N + I_{int} , \quad (3)$$

where

I_R = intensity of Rayleigh electronic scattering
I_N = intensity of nuclear scattering
I_{int} = interference term .

The intensity represented by the last two terms I_N and I_{int}, is a function of the source velocity.

It is quite clear that the variation of the scattering amplitudes with angle of scattering for two of the terms on the right-hand side of equation (3) will be different and at some values of $\sin \theta / \lambda$ becomes negligible as the atomic scattering factor (f_{R_j}) is reduced. At the same time I_N remains constant (apart from polarization effects) because of the constancy of the cross section of nuclear scattering.

On this ground we shall consider that the contribution even for 'heavy' atoms at large scattering angles will be small and equation (3) will be $I(H,S) = I_N$; that is, only the nuclear scattering will be registered. This feature is used in experiments on the Mössbauer effect when it is necessary to avoid the additional contributions in the background, for instance, of X-ray or harder γ radiation so as to increase the relative magnitude of the effect. By putting the system off resonance we may observe the Rayleigh scattering alone, that is I_R. Depending on the conditions of the experiments for the reflexions of the H type we can get the following information:

(1) $I(H,S) = I_R + I_N + I_{int}$
(2) $I(H,S) = I_R$
(3) $I(H,S) = I_N$
(4) $I(H,S) = I_{int}$ (4)
(5) $I(H,S) = I_R + I_N$.

Black (1965), on the basis of careful analysis, has shown how investigation of the separate terms in equation (3) may be used for determining signs and phases in crystals.

The peculiarity of 'Mössbauerography' is that each diffraction maximum (H) may have an additional fine structure (split line) which arises if scattering nuclei are in magnetic or anisotropic electric fields of the crystal. The relative intensity of the fine structure of the Bragg maximum is defined by the angle dependence of the direction of γ ray scattering on the tensor axis of the electric field gradient. The analysis of the diffraction maxima with fine structure of magnetic splitting contains information about the magnetic structure of the crystal.

The general principles of the theory of nuclear resonant scattering of γ radiation have been discussed by Trammell (1962), Kastler (1960), Podgoretskij & Stepanov (1961), Lipkin (1961), Kazarnovskij & Stepanov (1962). Tzara (1961) has calculated cross sections of the resonant scattering in the presence of coherent processes. Wong (1965) has also calculated the dependence of the Mössbauer scattering cross sections of circular polarized rays on the scattering angle for both split and unsplit lines.

Much attention has been paid to the problem of the interference between Rayleigh and nuclear scattering. Moon (1961) and Lipkin (1961) have predicted the vanishing of interferential term I_{int} at exact resonance, i.e. $I(H,S) = I_R + I_N$.

The greatest success in the classical theory of the Mössbauer type nuclear resonant and Rayleigh scattering taking into account interference effects was achieved by O'Connor & Black (1964); earlier work was published by Black & Moon (1960), and Black, Evans & O'Connor (1962). The corresponding tests in experimental observation $I(H,S)$ were made by Black & Moon (1960), Black, Longworth & O'Connor (1964), and also by Major (1961), who confirmed this theory.

Direct observation of coherent scattering in the absence of Rayleigh scattering was made by Black & Duerdoth (1964, 1966) on potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$.

The problem of the possible application of partial coherency of Bragg scattering on electronic shells and nuclei to structural analysis was first noted by Moon (1960) and Raghavan (1961). Later on different aspects of crystal structural applications of the Mössbauer effect were examined by Cormack (1963), Black (1965), and Kuz'min, Kolpakov & Zhdanov (1966).

All the above mentioned investigations aroused great interest in the processes of scattering of resonant γ quanta. Quite a few experimental investigations on the diffraction of Mössbauer γ quanta show, however, great difficulties in the realization of such experiments. The main obstacles in this problem are the small activity of γ ray sources and the inadequacy of radiation detection systems. If we remember the slow development of neutron diffraction, in which the main lines of advance became clear only after improvement of the methods of investigation, it can be supposed that a similar course may be followed in the case of Mössbauerography. Perhaps the greatest success at the present stage can be attained by applying a semiconductor detector and resonant detectors which are selectively sensitive to recoil-free γ rays (Mitrofanov, Illarionova & Spinel, 1963; O'Connor, Butt & Chohan, 1964; Owens; 1964; Mitrofanov & Rohlov, 1966).

Finally mention should be made of the Afanasiev-Kagan effect. Afanasiev & Kagan (1965a) showed that in some cases in the process of resonant γ-ray scattering in ideal crystals under the Bragg condition a situation can arise in which the amplitudes of formation of compound nuclei in the incident and diffracted waves are equal in value but opposite in sign. As both waves are coherent the probability of the formation of compound nuclei equals zero, thus causing the disappearance of inelastic channels of scattering so that the crystal becomes non-absorbing. Unfortunately there are no experimental facts which prove this effect. In the diffraction of X-rays the same phenomenon is known as the Borrmann effect (Borrmann, 1941, 1950); this appears in Bragg scattering from any crystal plane and is associated with anomalous transmission of X-rays. The Borrmann effect is caused by reduction in the absorption in the crystal because of interaction of the radiation with the electrons. The theory of the effect was developed by Laue (1949, 1952).

The possibility of observation of Mössbauer diffraction and the anomalous transmission of γ quanta and X-rays is very closely connected with the problem of the creation of a γ- or X-laser (Chiricov, 1963); Zagoretskij & Lomonosov, 1965; Afanasiev & Kagan, 1965b; Bond, Dugnay & Pentzepis, 1967).

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