SOVIET PHYSICS USPEKHI VOLUME 12, NUMBER 2 SEPTEMBER-OCTOBER 1969

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DIRECT DETERMINATION OF THE MAGNETIC STRUCTURE OF CRYSTALS WITH THE AID OF THE MOSSBAUER EFFECT

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Usp. Fiz. Nauk 97, 743–746 (April, 1969)

THE discovery of the Mossbauer effect has provided the physicists with an exceedingly powerful and strikingly universal research method. The range of application of this method extends from investigations of the fundamental physical laws (verification of general relativity, investigation of fundamental laws of symmetry and physics) to a solution of obviously practical and engineering problems (rapid determination of the percentage content of a chemical element in an ore, control of the rate of approach of artificial objects in outer space). In spite of the wide application of this effect in physical research, its capabilities are at present far from being fully exploited. An illustration of this statement is the present note. We report here the possibility of directly investigating magnetic crystal structures with the aid of the Mossbauer effect, to which attention was called in a theoretical paper.[1] The method proposed in [1] is the analog of magnetic neutron diffraction study, and is based on the dependence of the amplitude of the Mossbauer scattering of γ quanta on the direction of the magnetic field at the scattering nucleus.

Before we describe in greater detail the gist of the discussed method, let us remind the reader of some information concerning the Mossbauer effect. The Mossbauer effect is a phenomenon with the aid of which it is possible to obtain and detect nuclear γ radiation with a line width close to the natural width of the γ lines. This means that the corresponding γ radiation, the energy of which E_γ is usually of the order of several dozen keV, has a line width $\Gamma \sim 10^{-6}$–10^{-10} eV. It is precisely the combination of these two properties of the Mossbauer radiation, namely the narrowness of the line and the high energy, i.e., the smallness of the radiation wavelength, which explains its extensive utilization in physical research. The same qualities of the Mossbauer radiation determine also the possibility of directly investigating with its aid the magnetic structures of crystals. The narrowness of the line makes it possible to resolve the Zeeman splitting of nuclear levels in crystalline fields, i.e., it determines the sensitivity of the method with respect to magnetic fields, and the low wavelength $\lambda \lesssim 10^{-8}$ cm makes it possible to observe the diffraction of the Mossbauer radiation on crystals, i.e., to carry out a direct investigation of their structure. To confirm the foregoing, we present the parameters of the most widely used Mossbauer γ transition in ^{57}Fe:

$$E_\gamma = 14.4\ \text{keV},\ \Gamma \approx 10^{-8}\ \text{eV},\ \frac{\Gamma}{E_\gamma} \approx 10^{-12},$$

the lifetime of the excited state is $\tau_\gamma = 10^{-7}$ sec.

Mossbauer radiation is usually detected with the aid of resonant absorption. In view of the narrowness of the line of the Doppler shift of the γ-radiation energy, motion of the γ-ray source absorber at a speed on the order of 0.1–1 cm/sec suffices to violate the resonant-absorption condition. Figure 1a shows a typical Mossbauer absorption spectrum. It represents the γ-radiation intensity I passing through the absorber as a function of the velocity of the radiation source v relative to the absorber. This plot pertains to the case when the Mossbauer nuclei in the absorber are not situated in magnetic fields strong enough for Zeeman splitting of the nuclear levels, and the source line is not split. The conditions for resonant absorption by individual Zeeman transitions are satisfied at certain "resonant" values of the velocity v. The minima of the intensity transmitted by the absorber correspond on the diagram precisely to these velocities. Besides the resonant absorption, resonant scattering of the Mossbauer radiation is observed, and also its diffraction by the crystal structure.[2,3] A plot of the dependence of the intensity of the scattered radiation on v, for the same source and scatterer (absorber) as used to obtain Fig. 1a, is shown in Fig. 1b. Now the "resonant" values of the velocity v correspond to the scattering maxima. The magnetic ordering in crystals is usually investigated with the aid of the Mossbauer effect by using the dependence of the character of the Mossbauer spectrum of a single-crystal absorber (scatterer) on the direction of the external magnetic field in which the crystal is situated. If the intensity of the external magnetic field is comparable with the intensity of the crystal fields, then, by changing its direction, it is possible to estimate the orientation of the crystal magnetic fields relative to the external field from the change of the nuclear Zeeman splitting, which is manifest in the change of the distance between the minima (maxima) on Figs. 1a and b, i.e., it is possible to draw conclusions concerning the magnetic structure of the crystals.

In [1] we proposed a direct method for determining the magnetic structure of a crystal, based on an analy-

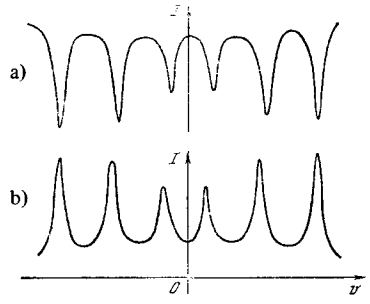

FIG. 1.

sis of the diffraction pattern occurring in resonant scattering of Mossbauer radiation by single crystals. It turns out that "magnetic" Bragg maxima exist in the Mossbauer scattering in the presence of magnetic ordering in the crystal. If the unit cell of the magnetic structure differs from the crystal unit cell, then purely "magnetic" maxima exist. Their occurrence is connected only with the dependence of the Mossbauer scattering amplitude on the direction of the magnetic field at the scattering nucleus, and their positions do not coincide with the positions of the crystalline maxima. We recall that x-ray scattering with an amplitude independent of the magnetic ordering cannot yield information concerning the magnetic order. The polarization of the Mossbauer radiation at the Bragg maxima contains information on the orientation of the magnetic fields at the Mossbauer nuclei relative to the crystallographic directions. We emphasize that with the aid of diffraction Mossbauer radiation it is possible to determine in a direct manner the structure made up by the magnetic crystal fields at the Mossbauer nuclei, and not the magnetic structure of the crystal in the customarily accepted meaning of the word. However, a direct determination of the ordering of the magnetic fields at nuclei is equivalent in many respects to a direct determination of the magnetic structure of the crystal, i.e., of the ordering of the magnetic moments of the atoms, since it is precisely the latter which causes the ordering of the magnetic field at the nuclei.

Let us explain the cause of the dependence of the amplitude of the Mossbauer scattering on the direction of the magnetic field at the scattering nucleus. By virtue of the long lifetime of the Mossbauer levels, the resonant scattering process can be divided into two stages: 1) resonant absorption of the γ quantum, which excites the nucleus to an intermediate excited state; 2) emission of a γ quantum by the excited nucleus; this returns the nucleus to the ground state. If the nucleus is in a magnetic field that causes Zeeman splitting of the nuclear levels, and the Mossbauer scattering is analyzed at a source velocity v corresponding to a definite Zeeman transition between the multiplets of the ground and excited states of the nucleus (to a definite maximum on Fig. 1b), then this means that the intermediate state of the scattering is characterized by a fully defined value of the nuclear spin projection on the direction of the magnetic field. Thus, the spin of the nucleus in the intermediate state turns out to be oriented in a definite manner relative to the direction of the magnetic field. In order to verify now that the scattering amplitude depends on the magnetic field direction, it suffices to consider the second stage of the scattering, and to recall that the probability of emission of a γ quantum by a polarized nucleus in a certain direction depends on the angle between this direction and the polarization axis. Figure 2 shows the dependence of the radiation intensity I on θ, the angle between the direction of the radiation in the magnetic field, for a dipole transition with a zero change in the projection of the magnetic spin on the field direction ($\Delta M = 0$).

We now proceed to the simplest model of resonant scattering, which describes quantitatively the foregoing qualitative considerations. Let a monochromatic beam of γ quanta be scattered elastically and resonantly from

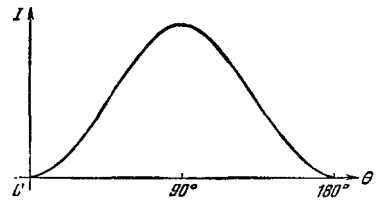

FIG. 2

a single crystal containing a Mossbauer isotope, and let the magnetic ordering in the crystal produce at the nuclei magnetic fields sufficient to split the Mossbauer radiation into individual Zeeman components. We assume that the crystal is ideal, the content of the Mossbauer isotope is 100%, and the nuclei have zero spin in the ground state and are rigidly secured at the lattice sites. The foregoing assumptions denote that the elastic scattering is fully coherent and that the Mossbauer factor is f = 1. Assuming also that the crystal is sufficiently thin, we neglect extinction. In the case of a fully polarized beam of primary γ quanta, the polarization of which is specified by a polarization vector $\mathbf{n}$, the cross section of elastic resonant scattering, corresponding to a final polarization described by polarization vector $\mathbf{n}'$, is of the form

$$\frac{d\sigma(\mathbf{k}, \mathbf{n}; \mathbf{k}', \mathbf{n}')}{d\Omega_{\mathbf{k}'}} = A\left|\sum_m f_m(\mathbf{k}, \mathbf{n}; \mathbf{H}_m; \mathbf{k}', \mathbf{n}')\, e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}_m}\right|^2 \sum_\tau \delta(\mathbf{k}-\mathbf{k}'-\tau), \quad (1)$$

where $\mathbf{k}$ and $\mathbf{k}'$ are the wave vectors of the initial and scattered γ quanta respectively, $\mathbf{H}_m$ is the magnetic field of the nucleus situated at the m-th lattice site, f_m is the amplitude of the Mossbauer scattering of the γ quanta for the m-th site, A a factor which is of no further importance, $\tau = 2\pi\mathbf{b}$, and $\mathbf{b}$ is the reciprocal-lattice vector of the crystal. In expression (1), m denotes the index of summation over the sights containing the Mossbauer-isotope nuclei, within the limits of one unit cell of the crystal, and $\mathbf{r}_m$ is the vector determining the position of the m-th sight.

Let us stop for simplicity to discuss the case when the magnetic fields at the Mossbauer nuclei can differ only in the direction, i.e., $|\mathbf{H}_m|$ does not depend on m. In this case, the resonant velocities of the source relative to the scatterer are the same for all m. If the amplitude f_m were to be independent of the direction of the magnetic field, as is the case for x-ray scattering, then regardless of whether ordering of the magnetic fields at the nuclei exist or not, the diffraction pattern described by expression (1) would be determined by the unit cell of the crystal structure. In the presence of ordering of the magnetic field at the nuclei, owing to the dependence of the direction of the magnetic field, formula (1) gives additional interference maxima, if the dimensions or the symmetry of the magnetic unit cell differ from the corresponding values of the crystal cell. We emphasize that the position of these maxima does not coincide with the position of the maxima of the Rayleigh scattering.

We now write out the explicit form of the amplitude of Mossbauer scattering from a nucleus placed in the magnetic field, for the case of a split scatterer line. Using the results of [4], we write the amplitude of the elastic Mossbauer scattering in the form

$$f(\mathbf{n}, \mathbf{k}; \mathbf{H}; \mathbf{n}', \mathbf{k}') = C(\mathbf{n}^*\mathbf{n}_0)(\mathbf{n}'\mathbf{n}_0)\sqrt{II'}. \quad (2)$$

where $\mathbf{n}$ and $\mathbf{n}_0'$ are the polarization vectors of γ quanta with wave vectors $\mathbf{k}$ and $\mathbf{k}'$, emitted by the scattering nucleus situated in a field $\mathbf{H}$, in a transition that is the inverse of the absorbing transition; I and I′ are the radiation intensities of the corresponding γ quanta, C is a factor of no importance to us. The dependence of the right side of Eq. (2) on H is via n_0, n_0^*, I, and I′. At the Bragg maximum, we obtain with the aid of (1) and (2) the following expression for the polarization of a γ quantum scattered by the crystal in pure Mossbauer fashion:

$$\mathbf{n}' = \frac{\sum_e \mathbf{n}_{e0}'(\mathbf{n}\mathbf{n}_{e0}^*)\sqrt{I_e I_e'}\, e^{-i(\mathbf{k}-\mathbf{k}')\mathbf{r}_e}}{\left|\sum_e (\mathbf{n}_{e0}'\mathbf{n}_{e0}^*)\sqrt{I_e I_e'}\, e^{-i(\mathbf{k}-\mathbf{k}')\mathbf{r}_e}\right|}. \quad (3)$$

The notation in (3) is the same as in (1) and (2), and the index labels the quantities pertaining to l-th direction of the magnetic field. As follows from (3), information concerning magnetic ordering is contained also in the polarization of the scattered radiation. When an unpolarized beam is scattered, the polarization density matrix of the scattered radiation can be obtained from (3) by means of suitable averaging.

We have considered above the case of fully coherent scattering. As is well known, allowance for the factors that lead to partial incoherence (crystal defects, its thermal oscillations, the deviation from zero of the spin of the ground state of the scattering nuclei, etc.) does not change the foregoing results quantitatively.

To get an idea of the scale of the angles that determine the positions of the diffraction maxima in Mossbauer scattering, we present the values of the minimal Bragg angles for scattering of Mossbauer radiation with energy 14.4 keV from ^{57}Fe by single-crystal α-Fe_2O_3. The first two crystal maxima are located at the Bragg angles ~7.5 and 9°, and the first two magnetic maxima are at ~5 and 6°.*

At the present time, only one method of directly determining the magnetic structures has been realized, namely magnetic neutron diffraction. Moreover, there is a widespread opinion that this is the only possible method of directly investigating magnetic ordering in crystals. This is the reason for the interest in a method that encroaches on the monopoly of magnetic neutron diffraction. In this connection, naturally, the question arises of the merits of the discussed method, and of its advantages and shortcomings compared with neutron diffraction. Although the final conclusions concerning the prospects of the method in the investigation of magnetic structure would be premature prior to a thorough investigation of the Mossbauer diffraction by magnetically ordered crystals, nevertheless we can note some shortcomings and advantages of general character. Among the advantages are the selectivity of the method (its sensitivity only with respect to Mossbauer isotopes), which facilitates the investigation of complicated compounds. Another great advantage is the simplicity of the Mossbauer setup (for neutron diffraction investigations it is necessary to have at least a reactor!). The sensitivity of the method only to Mossbauer isotopes, noted above as an advantage, is at the same time also a serious shortcoming, since it limits the investigations only to structures containing Mossbauer isotopes. The small natural content of the corresponding Mossbauer isotope is a shortcoming in the case of many Mossbauer transitions.

On the whole, under definite conditions, the Mossbauer diffraction is expected to become an effective method for directly investigating the magnetic structures.

In conclusion we note that besides the dependence of the amplitude of the Mossbauer scattering on the direction of the magnetic field at the scattering nucleus, the scattering amplitude depends also on the gradient of the electric field at the nucleus in the presence of quadrupole splitting of the nuclear levels. The latter dependence may turn out to be useful in investigation of ferroelectric structures with the aid of Mossbauer-radiation diffraction.[5]

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A very recent communication[6] reports experimental observation of a magnetic diffraction maximum in Mossbauer scattering of γ radiation by single-crystal α-Fe_2O_3. The authors note that the presence of magnetic diffraction maxima in the Mossbauer scattering makes it possible not only to investigate the magnetic structure of the crystal, but also to study dynamic effects in Mossbauer diffraction.

*The authors are grateful to G. V. Smirnov for calling their attention to erroneous values given for these angles in [1].

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Translated by J. G. Adashko