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SYMMETRY IN THE NUCLEAR SOLID STATE PHYSICS

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Abstract—In this paper some group-theoretical methods are discussed, which may be used to study both the hyperfine fields on nuclei of crystals, and the interaction of the nuclear resonant radiation with these crystals. Several types of hyperfine fields structures are considered. They are: the structure formed by the magnetic fields on nuclei, the electric field gradients structure and the combined one. It is shown, that the application of colour groups and tensor representations of space groups is not suitable for the study of the structures considered. Tensor representation also makes it possible to determine a set of possible reflections in Mössbauer diffraction patterns.

In this paper we consider the group-theoretical methods, which may be used for the study both the hyperfine (HF) fields in crystals, and the interaction of the nuclear resonant radiation with them.

Nuclear resonant spectroscopy and diffraction enable us to investigate the structures formed by a crystal magnetic field and an electric field gradient (EFG) in the points of the orbit of a crystal space group, which are occupied by the Mössbauer isotope atoms. Further, we shall call them the (HF) fields structures. Their symmetry differs from the space symmetry for a crystal and can be studied with the help of some group-theoretical methods.

One of these methods is the application of the colour groups [1]. Colour groups were introduced for the description of the subjects, which possess some local physical properties besides the property of the spatial symmetry. (Local properties are the properties in the points of the space group orbit.) Traditionally the colour groups are used for the description of symmetry of the magnetic crystals. A symmetry of the HF magnetic fields structures is similar to a symmetry of the structures, formed by the atomic magnetic moments, so the colour groups may be used for its study. Usually $G^{(q)}$ and $G^{(w)}$ colour groups are utilized for this purpose. These groups are constructed in the following way [2] (according to Ref. [3] $G^{(w)}$ has $G^{(w_p)}$ and $G^{(w_q)}$ forms)

$$G^{(w)} = WG \subseteq P \sim G = (P \otimes P \otimes \cdots \otimes P) \textcircled{s} G,$$

$$G^{(q)} = QG \subseteq Q \textcircled{s} G,$$

where G is the classical symmetry groups, P and Q are the permutations groups.

Nuclear resonant methods enables us to study not only the magnetic fields in cyrstals, but also the EFG tensors

$$\left.\frac{\partial^2 \varphi}{\partial x_i \partial x_j}\right|_{\mathbf{r}=\mathbf{r}_s}$$

(φ is the electric field potential) in the points occupied by the Mössbauer isotope nuclei. The EFG structures are not colour in itself from Q—symmetry point of view. The distribution function of charges, which cause the EFG existence, is invariant under the transformations of the space group G, so in the crystallographically equivalent points of the unit cell these tensors have the same value, and the directions of their main axes are connected with each other with the help of $g \in G$ transformations.

It was shown in Ref. [4], that the EFG structures show their colour properties in the Mössbauer diffraction experiments. The observation of the extra quadrupole reflections in the Mössbauer diffraction patterns gives the evidence of the colour symmetry of the EFG structure. So, the symmetry of the EFG structures essentially differs from the magnetic one, which is colour in itself and shows its colour properties under diffraction of slow neutrons and resonant γ-quanta. It was shown in Ref. [4], that we study in the diffraction experiments the symmetry of the enlarged system: crystal + radiation. It is this system, which becomes colour when the EFG tensors exist on the

nuclei. To describe this symmetry it is necessary to use $G^{(p)}$ groups of Belov without colour translations. For example, the colour group, corresponding to the EFG structure in TeO_2 single crystal is $P4_1^{(4)}2_1^{(2)}2$.

Consideration of the combined structure of the HF fields, i.e. both the magnetic field and the EFG tensor on nuclei deserves the particular interest. Nuclei of the Mössbauer isotope interact with the two fields simultaneously, so the combined structure shows itself not as the superposition of two individual structures. If the main axes of the EFG tensors and the magnetic field vectors on some crystallographically equivalent nuclei are orientated in different ways in respect to each other, their eigenstates and eigenvectors do not coincide. In Ref. [5] the combined HF structure was considered from the point of view of colour symmetry. In this approach p or q operations of $G^{(p)}$ or $G^{(q)}$ groups change an angle θ between the magnetic field vector and the EFG main axes. It was shown, that $G^{(w_q)}$ groups must be used. For example, the combined HF structure in a crystal $ZrFe_2$ is described by the group $(Fd^{(2,1)}3_{[111]}E^{(3,1)}_{\langle 111\rangle}m^{(2,1)}_{\langle 111\rangle})_{[11\bar{2}24]}$. The colour operations are interpreted in a q-sense, because they change not only the atoms coordinates, but the angle θ too:

$$g^{(q)}\mathbf{r}_i^{(\theta)} = \mathbf{r}_j^{(\theta+\Delta\theta)},$$

where $\Delta\theta = 70°31'$ for $p \neq 1$ and $\Delta\theta = 0°$ for $p = 1$. p numbers the atoms in the tops of the tetrahedron.

Groups of multiple antisymmetry [6] also may be used for the description of the combined HF structures. This way is not suitable, because these groups may be reduced to colour groups [7].

The combined HF structure may be considered as the EFG structure in the magnetic field, supposing the magnetic field to be the external influence, which decreases the symmetry of the EFG structure in classical sense. However, the colour symmetry of this widen system does not decrease.

The symmetry of the combined HF structures shows itself in a different way in Mössbauer diffraction experiments. In this case the amplitudes of the resonant scattering of Mössbauer radiation corresponding to those nuclei, which have the equal nuclear eigenstates may not be equal to each other. On account of this inequality colour groups must be used. For example, the diffraction symmetry of the combined HF structure in a crystal $ZrFe_2$ is described with the help of the group $Fd^{(2)}3^{(3)}m^{(2)}$.

It is shown in Ref. [8], that the inequality of the sets of nuclear eigenstates corresponding to the crystallographically equivalent atoms may lead to the occurrence of extra reflexes in Mössbauer diffraction patterns. These reflexes are absent if only the magnetic field or the EFG tensor exist in the nuclei. In Ref. [8] the Mössbauer diffraction pattern, corresponding to a crystal $ZrFe_2$ was considered. $ZrFe_2$ is a ferromagnetic, in which the EFG main axes are directed along the third order axes of a crystal. The scattering amplitude for the reflections $0k0$ ($k = 2n$) in proportional to $F(\mathbf{H}) \sim 4_i(f_1 - f_2 + f_3 - f_4)$, where f_i are the amplitudes of resonant scattering of the Mössbauer radiation of the nuclei forming the tetrahedra. $F(02n0)$ is equal to zero, if the nonresonant scattering of the Mössbauer radiation or the scattering in the presence only the magnetic field on nuclei take place. The nuclear resonant absorption spectra in this case are the surperpositions of two structures with the different splitting of the resonant lines. One of these structures corresponds to the nuclei with $\theta = 0°$, another to the nuclei with $\theta = 70°31'$. In Ref. [8] it was shown, that if the difference between the resonant energy values $E_M^1 - E_M^2$ (E_M^1 corresponds to the nuclei with $\theta = 0°$, E_M^2—to the others) is more than the width of the resonant line, the Mössbauer diffraction patterns have to contain the reflexes $0k0$, $h00$, $00l$; $k(h, l) = 2n$.

Another type of combined reflections was considered in Ref. [9]. In some cases the different scattering amplitudes f_i correspond to the nuclei with the same splitting of the nuclear levels, so they are not equivalent in respect of the Mössbauer diffraction. In Ref. [9] the possibility of the combined reflexes observation in the Mössbauer diffraction pattern of $KFeF_4$ single crystal was considered.

If Ref. [10] just one more type of the HF structures with colour symmetry was considered. It is the EFG tensors structure in the crystals with a spatial modulation. Nuclear magnetic resonance (NMR) was used in Ref. [10] as an experimental method of investigation. It was shown, that an EFG structure is also modulated in these crystals. If a spatial modulation is incommensurate, the EFG tensors in the centres of a crystal lattice differ from each other. In this work the conception of a colour modulation cell was introduced. Its length coincides with a modulation wavelength.

The authors have shown the element of the basic structure to be conserved in the colour symmetry sense. The calculations were made for the family of crystals K_2SeO_4. Before the phase transition the symmetry of the EFG structure was described by the group $P2_1/c\,2_1/m\,2_1/n$. After the transition this group transforms to $P_{c^{(3)}+\delta^{(w)}}2_1^{(2)}/c\,2_1/m^{(2)}2_1^{(2)}/n$.

The application of the colour symmetry groups is not the only way of describing the structures, which possess the local physical properties with certain symmetry. The alternative methods are the superspace groups [11, 12] and the space group representation method [3, 13].

Superspace groups were constructed for the description of the modulated structures. These groups consist of the elements

$$g_s = (g_E, g_I) = (\{R_E|\,V_E\}, \{R_I|\,V_I\}) \in E(3) \otimes E(d_0),$$

which act in a space with $3 + d_0$ dimensions. The index E corresponds to the external "geometric" space, I denotes the values in the internal space of the atomic displacements. The electron's density in these crystals is not invariant under the elements of the space group G, but it is invariant under the elements g_S: $\rho_0(\mathbf{r}) = \rho_0(g_S^{-1}\mathbf{r})$.

In Ref. [14] the superspace groups of symmetry were compared with the colour goups and their principal equivalence was shown. However, in each individual case one of these approaches may be preferable. When we describe the HF fields structure, we cannot give to g_I operations such a clear physical interpretation, as in a case of modulated structures. So in this case an application of colour groups is more preferable.

In Ref. [3] the group-theoretical approach was developed, in which the irreducible representations of space groups are utilized for the description of complex structures. The permutational, mechanic and magnetic representations were constructed. The main difference between them is a character of the basic functions. Scalar functions correspond to the permutational representation, vector functions to the mechanic representation and pseudovector to the magnetic one. All these representations are reducible and they may be expanded into a set of the irreducible representations of a space group. This method was applied in Refs [3, 13] to the consideration of phase transitions and to some problems of magnetic neutronography. It is well known, that neutron scattering in crystals is described by a vector function $\mathbf{F}(\mathbf{H})$, so the magnetic representation may be used for a study of $\mathbf{F}(\mathbf{H})$ properties. It was shown in Ref. [3] that $\mathbf{F}(\mathbf{H})$ may be represented in the following way:

$$\mathbf{F}(\mathbf{H}) = \sum_L \mathbf{F}^L(\mathbf{H}) \sum_n \exp[-i(\mathbf{H} - \mathbf{k}_L)\mathbf{Z}_n],$$

$$\mathbf{F}^L(\mathbf{H}) = \sum_{\lambda,j} C_\lambda^\nu \exp(-i\mathbf{H}\mathbf{r}_j) f_j(\mathbf{H}) \mathbf{S}(^{k\nu}_{\lambda}|j),$$

where $\mathbf{S}(^{k\nu}_{\lambda}|j)$ are the basic functions of the magnetic representation, C_λ^ν are the mixing coefficients, $\mathbf{k}_L$ is a vector of the magnetic structure, $\mathbf{H} = \mathbf{k} - \mathbf{k}_0$ is a vector of scatting, $\mathbf{k}_0$ and $\mathbf{k}$ being the wave vectors of the incident and the scattered radiations.

The magnetic representation of space groups certainly may be used for a study of HF magnetic structures on nuclei. As for EFG structures, we must utilize a tensor representation of a space group for its description. Some expressions for calculating the characters and the basic functions of this representation are given in Ref. [13]. In Ref. [15] it was shown, that the EFG tensor in the point of the space group orbit may be represented as:

$$\hat{\varphi}(\mathbf{r}_j) = \sum_\lambda C_\lambda^\nu \hat{\varphi}(^{k\nu}_{\lambda}|j),$$

where $\hat{\varphi}(^{k\nu}_{\lambda}|j)$ are the basic functions of the tensor representation corresponding to $\mathbf{k} = 0$ wave vector.

In contradiction to magnetic neutronography Mössbauer radiation scattering in the presence of HF field on nuclei has a tensor character, not depending on the kind of HF structure. In Ref. [16] it was shown, that a permittivity tensor formalism enables us to describe both transmission and diffraction of X- and γ-rays in crystals. The permittivity tensor may be represented as:

$$\epsilon_{ij}(\mathbf{k}, \mathbf{k}_0, \omega) = \sum_{\mathbf{H}} \epsilon_{ij}^{(\mathbf{H})}(\mathbf{k}, \omega)\delta(\mathbf{k} - \mathbf{k}_0 - \mathbf{H}),$$

where $\epsilon_{ij}^{(H)}$ are the diffraction components of the tensor. The polarizability $\chi_{ij} = (4\pi)^{-1}(\epsilon_{ij} - \delta_{ij})$ is connected with the scattering amplitude with the help of the expression

$$F(\mathbf{k}, \mathbf{e}, \mathbf{k}_0, \mathbf{e}_0) \sim e_i^* \chi_{ij}^{(H)}(\mathbf{k}, \mathbf{k}_0, \omega) e_j,$$

where $\mathbf{e}_0$, $\mathbf{e}$ are the polarization vectors of the incident and the scattered radiation. We have shown [17], that a proper representation from $\chi_{ij}^{(H)}$ may be constructed in a presence of the HF magnetic fields on nuclei as following:

$$\hat{\chi}^{M,(H)} = \sum_{\lambda\lambda' Lj} \exp(-i\mathbf{H}\mathbf{r}_j) C_\lambda C'_\lambda \mathbf{S}^M(^{kv}_{\lambda}|j) \cdot \mathbf{S}^M(^{kv}_{\lambda}|j).$$

This approach was utilized in Ref. [17] for the consideration of the peculiarities of the Mössbauer diffraction patterns of the crystals with a garnet type, which magnetic structure has $\mathbf{k} = 0$ wave vector.

The representation method is suitable for considering of Mössbauer diffraction in crystals with EFG on nuclei. In this case the $\chi^{(H)}$ tensors have a form:

$$\chi^{(H)} = \sum_{\lambda vj} C_\lambda^v \hat{\chi}(^{kv}_{\lambda}|j) \exp(-i\mathbf{H}\mathbf{r}_j),$$

where $\hat{\chi}(^{kv}_{\lambda}|j)$ are the tensor basic functions.

The application of the irreducible representations of space groups for a study of HF fields structures is possible due to isomorphism of colour and classical groups. The colour groups correspond to the permutational representation of space groups, because any colour may be identified with a number of a point of the space group orbit. So the colour groups and the representational methods are interrelated. Nevertheless the representation method is more preferable for the study of the HF fields structures, because, it allows to carry out some concrete calculations.

Utilization of tensor representation may apparently be the most useful for the consideration of Mössbaur diffraction patterns of crystals, when the combined HF structures or the nonaxial EFG attend on the nuclei. In these cases the calculations of the scattering amplitude is enough of a difficult problem, because the eigenvectors of the nuclear Hamiltonian have to be a mixing of the eigenvectors corresponding to certain magnetic quantum numbers. However, a tensor representation may be constructed easily in all the considered cases. Due to this representation we can state the possibility of some reflexes existence even when the EFG structures on the nuclei are not well known.

$KFeF_4$ [9] and YIG [19] were proposed to be the possible objects for the search of the combined reflections. Now some experimental investigations of the Mössbauer diffraction in the single crystals Fe_3BO_6 are carried out. These crystals have D_{2h}^{16} symmetry and the antiferromagnetic structure. The nuclei of the Mössbauer isotope Fe^{57} occupy 8(d) and 4(c) positions in a unit cell. In Ref. [18] some additional lines were observed in the energy spectra corresponding to the reflexes $00l(l = 2n + 1)$. The existence of these lines may be caused by the combined HF fields structure on the nuclei of Fe_3BO_6. If the EFG would be absent, these reflexes must be purely nuclear magnetic reflections. In this case the observed lines have to be absent. It is interesting to study this crystal to observe some more effects, for example the combined reflections under $T < T_N$ and the quadrupole reflections under $T > T_N$.

Using the approach considered above we have analysed the possibility of the quadruple reflections occurrence in the Mössbauer diffraction pattern of Fe_3BO_6 not attaining the data on the EFG structure, which is not well known yet. The calculations of the tensor modes show the possible extinctions of the quadrupole reflexes $h00$, $0k0$, $00l$; $h(k, l) = 2n + 1$ and existence the reflexes $0kl(k + l = 2n + 1)$.

Thus the utilization of the group-theoretical approaches leads not only to the better understanding of the observed phenomena, but in some cases simplifies the theoretical calculations.

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