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High-resolution spectroscopy of crystals containing transition metal ions (review)

© M.N. Popova

Institute of Spectroscopy, Russian Academy of Sciences, 108840 Troitsk, Moscow, Russia

e-mail: popova@isan.troitsk.ru

A brief review of studies of crystals containing metal ions with unfilled f- or d-shells, made in the Institute of Spectroscopy of the Russian Academy of Sciences by high-resolution Fourier spectroscopy, is given. The main directions of study include hyperfine structure in spectra, isotopic effects, the role of random deformations, phase transition spectroscopy, low-dimensional magnets, coupled electron-phonon excitations.

Keywords: High-resolution Fourier spectroscopy, crystals with f- and d-ions, hyperfine structure, isotope effects, phase transitions.

Introduction

The review shows basic results of studies of crystals containing metal ions with unfilled f- or d-shell, obtained in the Institute of Spectroscopy of RAS (ISAS) by high-resolution Fourier spectroscopy. This method has been developed in ISAS from the very foundation of the Institute in 1968, on the initiative of Sergey Leonidovich Mandelstam, the first director of ISAS. In cooperation with the Central Design Bureau for Unique Instrumentation (CDBUI) of the Academy of Sciences of the USSR the unique high-resolution Fourier spectrometers UFS-01 and UFS-02 were designed and installed in ISAS. Employees of ISAS and CDBUI G.N. Zhizhin, E.A. Vinogradov, A.A. Balashov, V.S. Bukreev, N.G. Kultepin, V.A. Vagin, I.N. Nesteruk, E.B. Perminov participated in this work. The infrared vacuum Fourier spectrometer UFS-02 operated in the range from 50 to $0.8\,\mu m$ with a resolution up to $0.005\,cm^{-1}$. Spectrometers of this class at that time were only in France, where they were used to study atomic and molecular spectra. It was decided in ISAS for the first time in the world to use high-resolution Fourier spectroscopy for the study of condensed mediums. In 1985 spectra were demonstrated that could not be obtained by any other method, namely, the spectra of $LiYF_4$:Ho crystal with a resolved hyperfine structure [1]. Since then, various crystals have been systematically studied in ISAS by high-resolution Fourier spectroscopy. Currently, ISAS operates the Unique Scientific Facility „Multifunctional Wide-Range High-Resolution Spectroscopy" (USF MWHRS ISAS) [2], which is based on a Bruker 125HR high-resolution Fourier spectrometer. K.N. Boldyrev, S.A. Klimin and other employees of the Laboratory of Fourier Spectroscopy of ISAS significantly expanded the capabilities of the commercial device. Using USF it is possible to record the spectra of transmission, reflection, luminescence, diffuse transmission and reflection, ATR (including those in polarized light, in magnetic fields) in the range of $15-30\,000\,cm^{-1}$ (from terahertz to ultraviolet) with resolution up to $0.001\,cm^{-1}$ in the entire spectral region. Temperature range: from $\sim 1.6\,K$ (helium pumping out) to $\sim 450\,K$ (heating attachment).

Research in the ISAS Laboratory of Fourier Spectroscopy is carried out in collaboration with theorists (mainly the group of B.Z. Malkin at the Kazan Federal University) and many Russian and foreign scientific institutions. There are several main areas of research. I.e. hyperfine structure in spectra, isotopic effects, the role of random deformations, phase transition spectroscopy, low-dimensional magnets, coupled electron-phonon excitations.

Studies of hyperfine interactions

In the papers [1,3–14], the hyperfine structure was registered and studied in the spectra of a number of crystals activated by rare-earth (RE) ions. These works, which at first seemed purely academic, turned out to be in demand in connection with the occurrence and intensive development in the last decade of a new field of science, i.e. quantum informatics. Various optical quantum memory devices are being developed for quantum repeaters in communication lines based on quantum cryptography, for quantum computers. The overwhelming majority of already working laboratory prototypes of optical quantum memory is based on hyperfine levels of RE ions in crystalline matrices. The active search for new ion−matrix combinations is performed. In this connection, studies of the hyperfine structure in the spectra of materials promising for optical quantum memory are actual.

Isotopic effects

The fine structure of the hyperfine line components in the absorption spectra of impurity holmium ions in crystals

of lithium-yttrium double fluorides, $LiYF_4 : Ho$, was found in the paper [15]. It was experimentally proved that this structure in the spectra of the single-isotope element of holmium is due to isotopic disorder in the lithium sublattice, and that the crystal field acting on Ho^{3+} ion depends on the lithium isotope composition in the nearest environment of Ho^{3+} ion. Due to the difference in the masses of ^6Li and ^7Li isotopes, the amplitudes of their vibrations differ, and due to the anharmonicity of zero vibrations, this leads to a shift in the equilibrium positions of the nearest fluorine ions. Theoretical consideration (B.Z. Malkin) showed that specifically this mechanism of lattice static deformation prevails in the isotopic structure formation in comparison with the dynamic effect due to electron-phonon interaction [16]. The isotopic structure associated with the isotopic disorder in the lithium sublattice in $LiYF_4$ crystal was also discovered and studied in the electronic spectra of other impurity ions: erbium [6,17] and thulium [10,11]. The developed theory was also used to interpret the reflection spectra of crystals of lithium-yttrium double fluorides with different contents of lithium isotopes, $^6Li_x \,^7Li_{1-x}YF_4$ [18]. The paper [19] contains a brief review of our studies of hyperfine and isotopic structure in the optical spectra of crystals with RE ions.

These papers showed that isotopic disorder makes a significant contribution to the inhomogeneous splitting and broadening of spectral lines, and stimulated the use of isotopically pure crystals in modern quantum informatics devices.

Inhomogeneous broadening and fine structure of spectral lines due to random deformations of the crystal lattice

The question of inhomogeneous broadening of spectral lines is a fundamental question of spectroscopy. In the classical paper by Stoneham [20], the shapes of inhomogeneously broadened lines of singlet-singlet transitions due to various types of defects were analyzed. In this and many subsequent papers a one-dimensional distribution function of random deformations in isotropic continuum was used. Such an approach is obviously not suitable for describing the inhomogeneous broadening of the spectral lines of transitions between levels, at least one of which is orbitally degenerate, and in actual anisotropic crystals. In the high-resolution spectra of RE ions in crystal fields of cubic [21], tetragonal [11,22,23] and trigonal [24] symmetries, we found spectral lines with a specific dip in center corresponding to transitions involving orbitally degenerate electronic states. A microscopic theory of deformation broadening and splitting of spectral lines was developed, including the derivation of a generalized distribution function for the components of the random deformation tensor induced by point defects in elastically anisotropic continuum (B.Z. Malkin et al.) [23]. Measurements of the evolution of the line shape (width of the dips) with change in the concentration of RE ions made

it possible to obtain estimates of the strengths of defects caused by impurity ions in activated crystals [22,23]. The results of this series of works demonstrated the possibility of using the high-resolution spectroscopy to quantify the quality of optical materials and optimize their synthesis modes.

Rare-earth borates with huntite structure

A large cluster of papers relates to the study of compounds from an extensive family of functional borates with the structural type of the natural mineral huntite with the general chemical formula $RM_3(BO_3)_4$ (R = Y, La−Lu; M = Al, Ga, Fe, Cr, Sc). Huntites crystallize mainly in a non-centrosymmetric trigonal structure (optical nonlinearity, magnetoelectric properties) containing chains of MO_6-octahedrons connected by RO_6-prisms isolated from each other (small luminescence quenching of R^{3+} RE ions). These are wide-gap dielectrics. Such features, together with mechanical strength, good thermal conductivity, and chemical resistance, make these compounds promising for use as laser and nonlinear media up to ultraviolet. While aluminum borates are widely used in quantum electronics, gallium borates have been little studied. We have shown that their luminescent and nonlinear properties are comparable to those of aluminum borates [25].

Huntites with magnetic ions M^{3+} (Fe, Cr) have interesting magnetic properties. We investigated the entire range of RE ferroborates [26–39]. On the basis of information, obtained from the analysis of high-resolution spectra, about the energies and symmetries of the Stark levels of RE ions and their splitting during magnetic ordering the parameters of the crystal field and exchange interactions were found [26–32]. These parameters were used to simulate the magnetic broadening properties of RE ferroborates [26–32], the chiral structure of electric quadrupole moments [31] and to calculate the electric polarization [30]. At the same time, in order to take into account the quasi-one-dimensionality of the magnetic subsystem of iron, a model (B.Z. Malkin) of four-particle cluster of iron ions was developed — a minimal model that reproduces the properties of chain [33]. The effectiveness of various mechanisms of the magnetoelectric response of ferroborates was estimated. The measured characteristics of the high-resolution spectra, supplemented by calculations of the parameters of crystal fields and the Stark structure of RE ion multiplets, made it possible to determine the type of magnetic structure in the magnetically ordered phase of the studied compounds, and even in cases where it is impossible or difficult to study the magnetic scattering of neutrons [29,30]. The effect of chirality of field-induced magnetic moments in the paramagnetic phase of dysprosium ferroborate [31] is predicted. A new effect was discovered: the appearance of a new line in the absorption spectrum during magnetic ordering, which corresponds to a forbidden transition in praseodymium ferroborate [34]. Coupled electron-phonon excitations [35–38] were discovered

and studied. A new effect was discovered and explained, it was caused by resonant electron-phonon interaction in antiferromagnetic dielectric placed in an external magnetic field, namely, the formation of a gap in the spectrum of electronic excitations [37].

A recent paper [39] relates to the study of low-temperature structural and magnetic phase transitions in solid solutions $Eu_{1-x}La_xFe_3(BO_3)_4$. It is shown that the structural transition temperature and the width of the hysteresis loop can be controlled by changing x (composition), and a model is proposed to explain the experimental results. The situation is demonstrated when the structural transition temperature $(12\,K)$ is much lower than the magnetic ordering temperature $(32\,K)$.

Unlike ferroborates, huntites with another magnetic ion, Cr^{3+}, have been little studied. They are characterized by low-temperature phase transitions and, which greatly complicates studies, polymorphism with the presence of different structural phases in one crystal [40].

Low-dimensional and frustrated magnets

Many publications relate to the study of low-dimensional and frustrated magnetics: In terms of physics they are interesting, first of all, due to their unusual purely quantum properties. These are spin-Peierls transitions in chains of half-integer spins, the Haldane gap in the spectrum of magnetic excitations of chains of integer spins, the states of spin ice or spin liquid in frustrated magnets, and so on. We have carried out a number of studies on crystals with low-dimensional and/or frustrated magnetic interactions by high-resolution Fourier spectroscopy.

The papers [41–48] relate to investigation of phase transitions and crossover from one-dimensional to three-dimensional magnetism in the family of chain nickelates $Y_{2-x}R_xBaNiO_5$ (R — rare earth) — quasi-one-dimensional Haldane magnets (spin of ions Ni^{2+} $S = 1$). Whereas yttrium nickelate is an ideal one-dimensional magnetic (there is no magnetic ordering in it, at least down to $0.1\,K$, the Haldane gap is observed in the spectrum of magnetic excitations, which is characteristic of chains of integer spins), yttrium replacement by a rare earth leads to increased interchain interaction and three-dimensional magnetic order. Magnetic phase transitions were recorded, and the types of magnetic structures in R_2BaNiO_5 compounds were determined by the RE probe method [41–44,48]. Comparison of the measurement data with the results of calculations in the developed by B.Z. Malkin model of exchange charges in the theory of the crystal field made it possible to conclude that the type of magnetic structure is determined by the single-ion magnetic anisotropy of the RE ion [45,46]. A new type of optical excitation of one-dimensional chain of spins $S = 1$ (magnetic absorption with the participation of a phonon) was discovered in the infrared spectra of chain gadolinium nickelate [47]. Using the results of calculations

of the lattice dynamics, a possible mechanism for the formation of spin-phonon excitations is considered [47].

The papers [49–57] present the results of spectroscopic studies of the spin-Peierls quasi-one-dimensional magnetic $CuGeO_3$ and the compound NaV_2O_5, in which a complex phase transition similar to the spin-Peierls transition, and accompanied by charge ordering is observed. In the papers [58,59] based on spectroscopic data for $Yb_2Ti_2O_7$, the parameters of the crystal field for frustrated magnets with the pyrochlore structure $R_2Ti_2O_7$ were analyzed (R = Tb, Ho, Er, Tm, Yb). Physically justified correct parameters are needed to interpret the low-temperature magnetic structure and spin dynamics of pyrochlores. The papers [60–62] relate to the first results of the study of new magnetic compounds $Ln_3CrGe_3Be_2O_{14}$ (Ln = La, Pr, Nd) with quasi-one-dimensional interactions in the chromium subsystem and frustrated interactions in the RE subsystem. This is the first example of compounds from the langasite functional family in which two magnetic subsystems are present.

Another extremely interesting magnetic compound should be mentioned, i.e. copper metaborate CuB_2O_4, which has a tetragonal crystal structure. Despite the simple formula, the structure is complex, with 12 formula units per unit cell and two non-equivalent positions for copper ions Cu^{2+}. In this case, in one of the copper subsystems the one-dimensional magnetic interactions prevail, and it remains disordered at the lowest temperatures. The second copper subsystem is ordered at temperature of $20\,K$, it is characterized by an extremely complex phase $H-T$-diagram. In our paper [63] we discovered optical linear dichroism appearing during magnetic ordering in the isotropic crystallographic base plane of the copper metaborate crystal. The nature of linear dichroism was identified, and it is shown that it can serve as a sensitive, sublattice-selective method for detecting phase transitions and probing magnetic structures. The paper [63] also finalizes the fundamental discussion about the possibility to monitor the chirality of the crystal with the help of the magnetic field.

Conclusion

The possibilities of studying condensed matter by high-resolution Fourier spectroscopy go beyond the areas discussed. Interesting results were recently obtained at ISAS relating the physics of hybrid organic-inorganic perovskites, various impurity centers in diamond and silicon, and magnetostructural phase transitions in a number of compounds.

Conflict of interest

The author declares that she has no conflict of interest.

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