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Mössbauer spectroscopy of ^{67}Zn impurity atoms in lithium and rubidium halides

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Abstract. Central shifts of the Mössbauer emission spectra on impurity atoms ^{67}Cu(^{67}Zn) in the crystal lattices of lithium and rubidium halides are determined. Relativistic Doppler shifts of the spectra are calculated and, as a result, isomeric shifts are obtained. The are compared with the nature of the chemical bond of zinc atoms with halogen atoms in the crystals under study. The values of the quadrupole interaction constants for zinc impurity centers in lithium and rubidium halide are consistent with the values obtained in the ionic model calculations.

Keywords: crystals of lithium and rubidium halides, impurity zinc atoms, Mössbauer spectroscopy, relativistic Doppler shifts, isomeric shifts, central shifts

Introduction

One of the advantages of Mössbauer spectroscopy (MS) is the ability to determine the valence and coordination states of the probe atom, as well as the symmetry of its local environment, based on the values of the isomeric shift *(IS)* and quadrupole splitting *(QS)* of the spectrum. The Mössbauer isotope ^{67}Zn with an isomeric transition energy of 93.3 keV is of particular interest in this regard. Firstly, it has the smallest natural spectral line width of 0.32 μm/s among all other isotopes (the value of 3.1 microns/s has been experimentally achieved). Secondly, the high value of the spin of its ground state $I = 5/2$ makes it possible to extract complete information about the quadrupole interaction tensor of the nucleus from the experimental spectrum, i. e., its main value and the asymmetry parameter (Mitchell et al. 1993; Terukov et al. 2018).

However, it should be borne in mind that only the central shift *CS* can be determined directly from the experimental Mössbauer spectrum, which is the sum of the isomeric shift *IS* and the relativistic Doppler shift *DS*

$$CS = IS + DS. \qquad (1)$$

Thus, to determine the values of the isomeric shift of the Mössbauer spectra (MS) of ⁶⁷Zn, which carries basic information about the electronic structure of zinc centers, it is necessary to take into account *DS*, which significantly limits the practical use of MS on the ⁶⁷Zn isotope in solid state physics, since the calculation of *DS* for ⁶⁷Zn is still an unsolved theoretical problem. Attempts to use model vibrational spectra in theoretical calculations of *DS* (e. g., the Debye model) did not give satisfactory results (Forster et al. 1980) and, therefore, the authors (Mitchell et al. 1993), when studying oxides, chalcogenides and zinc fluoride by the MS method on the ⁶⁷Zn isotope, calculated the *DS* values for each compound using complex lattice-dynamic models. However, this approach can hardly be used for routine interpretation of spectra. In addition, such calculations will require even more complication in the case of impurity probe atoms.

In this paper, a Mössbauer study of ⁶⁷Zn impurity atoms in the crystal lattices of lithium and rubidium halides was carried out in order to obtain information simultaneously on the central, isomeric and Doppler shifts of the Mössbauer ⁶⁷Zn spectra. The principal possibility of calculating the quadrupole interaction constant for ⁶⁷Zn impurity centers in lithium halides LiHal and rubidium RbHal (Hal = F, Cl, Br, I) within the ion model of point charges is also demonstrated.

Experiments

The Mössbauer sources were prepared by diffusion of ⁶⁷Cu into lithium and rubidium halide tablets pressed from powders. For this purpose, a solution of the non-bearing $^{67}CuCl_2$ in 0.1 N HCl was applied to the surface of the tablet, which was then dried and annealed in halogen. The Mössbauer spectra of ⁶⁷Cu(⁶⁷Zn) were taken at 4.2 K with a ZnS absorber. The central and isomeric shifts are attributed to a ZnO absorber with a wurtzite structure at 4.2 K.

Results and discussion

The ⁶⁷Cu(⁶⁷Zn) spectra of all lithium and rubidium halide samples are quadrupole triplets corresponding to the centers of divalent zinc $^{67}Zn^{2+}$ (see Figs. 1 and 2). The parameter of asymmetry of all triplets turned out to be close to zero ($\eta_{exp} < 0.1$).

Fig. 1. Mössbauer emission spectra of ⁶⁷Cu(⁶⁷Zn) in lithium halides relative to the ZnS absorber. When measuring emission spectra, the direction of the velocity scale is rotated relative to the natural scale in such a way that higher values of the transition energy correspond to more positive velocities
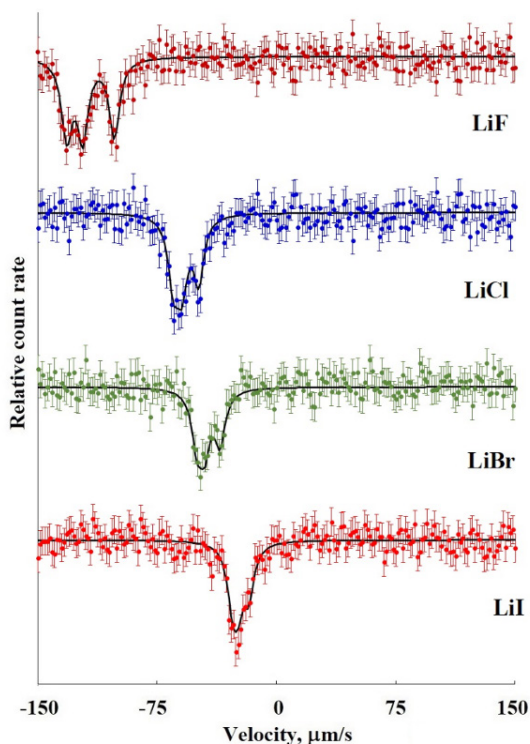
Fig. 2. Mössbauer emission spectra of $^{67}Cu(^{67}Zn)$ in rubidium halides relative to the ZnS absorber.
When measuring emission spectra, the direction of the velocity scale is rotated relative to the natural scale
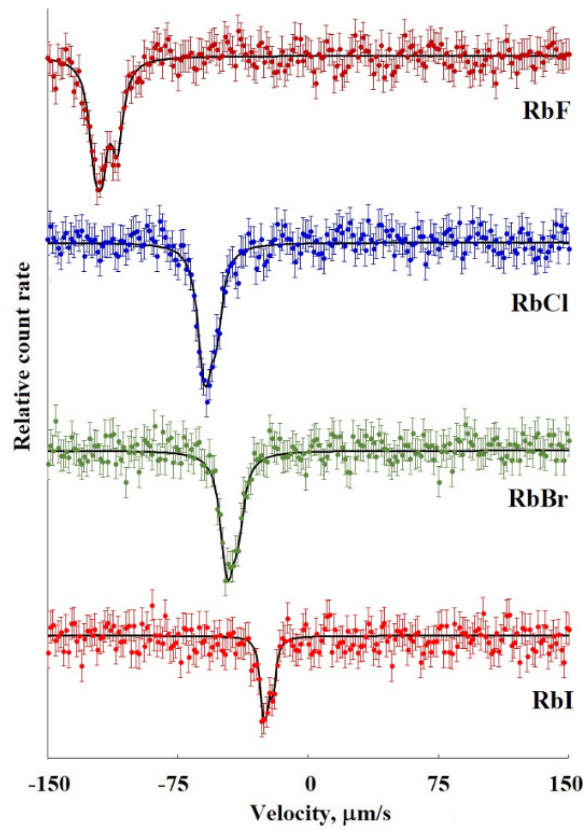in such a way that higher values of the transition energy correspond to more positive velocities

Apparently, halogen annealing of LiHal and RbHal samples doped with copper stabilizes the parent ^{67}Cu atoms in cationic positions in a divalent six-coordinated form, while the excess charge of $^{67}Cu^{2+}$ ions is compensated by cationic vacancies forming associates with Cu^{2+} centers. This leads to a decrease in the local symmetry of the $^{67}Zn^{2+}$ centers and, as a result, to the appearance of quadrupole splitting of the spectrum. This interpretation of the spectra is supported by the results reported in (Seregin et al. 2001). The study focused on the state of $^{67}Cu(^{67}Zn)$ impurity atoms introduced into AgCl crystals during diffusion doping in vacuum by Mössbauer spectroscopy and in the chlorine atmosphere. In the former case, Cu^+ centers appear in the nodes of monovalent silver and Mössbauer spectrum is a singlet line corresponding to $^{67}Zn^{2+}$ centers in an undistorted octahedral environment of chlorine atoms. In the latter case, Cu^{2+} centers appear in the nodes of monovalent silver and the spectrum is a quadrupole triplet, corresponding to $^{67}Zn^{2+}$ centers in a distorted octahedral environment of chlorine atoms due to the formation of associates with Cu^{2+} centers by cationic vacancies.

The dependence of the central shift of the $^{67}Cu(^{67}Zn)$ spectra for lithium and rubidium halides on the difference in the Pauling electronegativity for zinc atoms and Δx ligand atoms is shown in Fig. 3 (for octahedrally coordinated zinc centers, this difference is multiplied by a factor of 1.5 to take into account the greater number of nearest neighbors of the zinc atom).

We did not use calculations to find the values of the relativistic Doppler shift *DS*. Instead, we used empirical dependences $DS = f(\Delta x)$ for four and six coordinated zinc centers, established from the analysis of data on the values of *DS* and Δx for oxides, chalcogenides and zinc fluoride (Mitchell et al. 1993). The *DS* values obtained this way make it possible, using ratio (1), to determine the isomeric shifts of the *IS* of the Mössbauer spectra of ^{67}Zn impurity atoms in copper and sodium halides. Such *IS* estimates do not claim to be more accurate, since the authors (Mitchell et al. 1993) indicate errors of ± 8 miμ/s for the *DS* values calculated by them, but they allow us to identify trends in *IS*. Fig. 3 shows the dependence $IS = f(\Delta x)$, which indicate a linear correlation between the isomeric shifts of the Mössbauer spectra

of ^{67}Zn impurity atoms in the octahedral positions of the crystal lattices of lithium and rubidium halides and the degree of ionization of the chemical bond of zinc and chalcogen atoms.
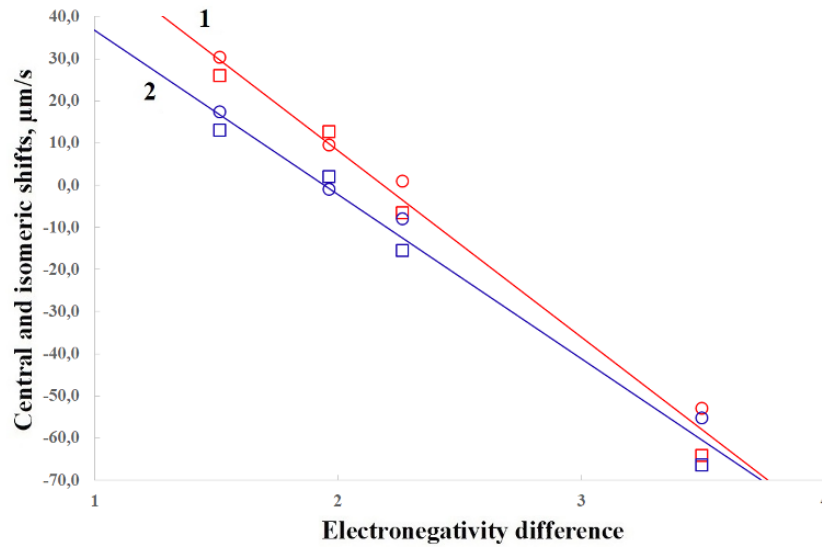

Fig. 3. Dependences of the central shift *CS* (line 1) and isomeric shift *IS* (line 2) relative to ZnO (wurtzite) from the difference of electronegativity of atoms for lithium halides (squares) and rubidium (circles)

The spatial localization of the cationic vacancy in the local environment of the $^{67}Zn^{2+}$ center can be established by comparing the experimental parameters of the nuclear quadrupole interaction (NQI) determined by the MS methods on the ^{67}Zn isotope and the parameters of the electric field gradient tensor calculated in the point charge model. The parameters of the NQI are the quadrupole interaction constant $C_{exp} = eQU_{zz}$ (here, eQ is the quadrupole moment of the probe core) and the parameters of the diagonalized electric field gradient (EFG) tensor on $^{67}Zn^{2+}$ probe cores in the crystal lattice are the main component U_{zz} and the asymmetry parameter $\eta = (U_{xx} - U_{yy})/U_{zz}$, where the components of the EFG tensor U_{xx}, U_{yy}, U_{zz} are related by the ratios $U_{xx} + U_{yy} + U_{zz} = 0$ and $|U_{xx}| \le |U_{yy}| \le |U_{zz}|$. In the general case

$$eQU_{zz} = eQ(1 - \gamma)V_{zz} + eQ(1 - R)W_{zz}, \quad \eta = (1/U_{zz})[(1 - \gamma)V_{zz}\eta_{lat} + (1 - R)W_{zz}\eta_{val}], \qquad (2)$$

where V_{zz}, W_{zz}, U_{zz} are the main components of the lattice, valence and total EFG tensors, $\eta_{lat} = (V_{xx} - V_{yy})/V_{zz}$, $\eta_{val} = (W_{xx} - W_{yy})/W_{zz}$ are the asymmetry parameters of the lattice and valence EFG tensors, γ and R are the Sternheimer coefficients that take into account the antishielding and shielding of the gap created by external charges or internal electron shells of the probe atom.

For probes with a fully (or half) filled valence shell $W_{zz} \approx 0$, the calculation of the lattice EFG tensor can be carried out using the point charge model. Since a regular lattice of the NaCl type does not create an EFG in its nodes, the cationic vacancy in the immediate environment of the Zn center was considered the only source of the EFG. The values of the main component of the lattice EFG tensor on zinc nuclei were calculated according to the ratio $V_{zz} = 2e^*/r^3$. Here, r is the Zn-vacancy distance equal to $r_1 = a_0/2^{1/2}$ or $r_2 = a$ for the first and second coordination shells, and a_0 is the lattice constant. The vacancy charge e^* was considered negative and equal in modulus to the electron charge. The asymmetry parameter of the EFG tensor in agreement with the experimental spectra was assumed to be 0 due to axial symmetry. Further, the experimental constants of the quadrupole interaction were compared with the contribution of the lattice gap $C = \alpha V_{zz}$, where $\alpha = eQ(1 - \gamma)$. Fig. 4 shows the calculated dependences $C = f(V_{zz})$ for Zn^{2+} centers in the LiHal and RbHal lattices, as well as experimental values of C.
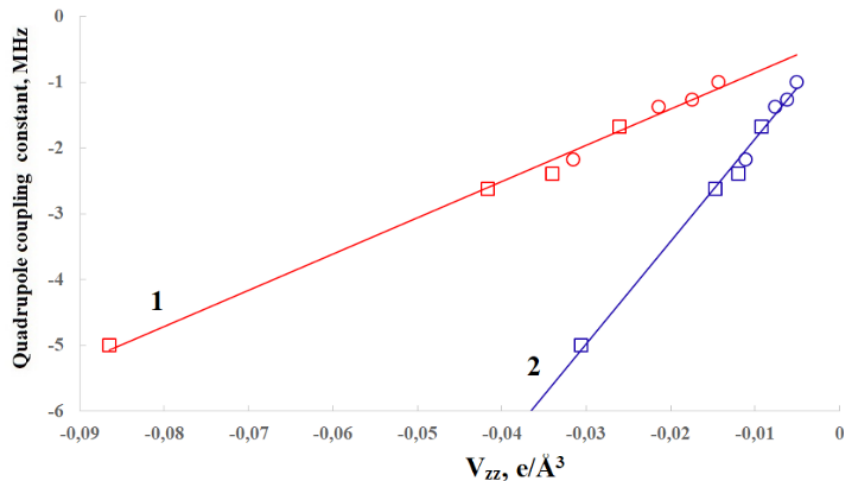
Fig. 4. Dependences of the quadrupole interaction constant on the main component of the lattice gap tensor V_{zz} for ^{67}Zn impurity atoms in lithium halides (squares) and rubidium (circles). Lines 1 and 2 correspond to vacancies in the first and second coordination spheres of impurity zinc atoms, respectively

Both dependences are linear, and it is possible to determine their angular coefficients α. For a vacancy in the first coordination shell α = (55 ± 1) $MHz \cdot Å$-3/e. If we take the value γ = −12.2 for the Sternheimer coefficient (Sternheimer 1966), then for the quadrupole moment of the nucleus ^{67}Zn we have Q = 0.12(3) b, which is in agreement with the data reported in (Bieroń et al. 2018; Pyykko 2008). For a vacancy in the second coordination shell, α = (156 ± 1) $MHz \cdot Å^{-3}/e$, which results in Q = 0.34(3) b. This differs significantly from the generally accepted values. The difference in the electrostatic energies of the Zn-vacancy pair $e^{2/4}\pi\varepsilon_0 r$ is 1–1.5 eV for r_1 and r_2 (0.16–0.25 eV, if we take into account the polarization of the medium using static permittivity). Apparently, this difference is sufficient to capture the vacancy during annealing at a minimum distance from the center of Zn.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors discussed the final work and took an equal part in writing the article.

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