

06.5

Investigation of sodium and copper halides by the method of Mössbauer spectroscopy on the isotope ^{67}Zn

© A.V. Marchenko¹, E.I. Terukov^{2,3}, F.S. Nasredinov⁴, V.S. Kiselev¹, P.P. Seregin¹

¹ Herzen State Pedagogical University of Russia, St. Petersburg, Russia

² Ioffe Institute, St. Petersburg, Russia

³ St. Petersburg State Electrotechnical University „LETI“, St. Petersburg, Russia

⁴ Peter the Great Saint-Petersburg Polytechnic University, St. Petersburg, Russia

E-mail: ppseregin@mail.ru

Received April 28, 2023

Revised May 20, 2023

Accepted May 23, 2023

The central shifts of the emission Mössbauer spectra on ^{67}Cu (^{67}Zn) impurity atoms in the crystal lattices of sodium and copper halides are determined, the relativistic Doppler shifts of the spectra are calculated, and, as a result, isomeric shifts are obtained, which are compared with the nature of the chemical bonding of zinc atoms with halogen atoms in the studied crystals. The values of the quadrupole interaction constants for impurity zinc centers in sodium halides are consistent with the results of calculating these values within the framework of the ionic model.

Keywords: alkali metal and copper halide crystals, impurity zinc atoms, Mössbauer spectroscopy.

DOI: 10.61011/TPL.2023.07.56453.19612

Mössbauer spectroscopy (MS) has an advantage in that the measured isomeric shift (IS) and the quadrupole splitting of a spectrum allow one to determine the valence and coordination states of a probe atom and the symmetry of its local environment. The Mössbauer ^{67}Zn isotope with an isomeric transition energy of 93.3 keV is of special interest in this regard. First, its natural spectral line width is the smallest among all isotopes: $0.32\ \mu\text{m/s}$ (a value of $3.1\ \mu\text{m/s}$ was achieved experimentally). Second, its ground state has high spin $I = 5/2$, which makes it possible to extract complete information on the tensor of quadrupole interaction of the nucleus (i.e., determine its principal value and asymmetry parameter [1,2]) from an experimental spectrum.

However, it should be understood that only the central shift (CS), which is a sum of IS and the relativistic Doppler shift (DS), may be derived directly from an experimental Mössbauer spectrum:

$$\text{CS} = \text{IS} + \text{DS}. \quad (1)$$

It was demonstrated experimentally and theoretically in MS studies that $\text{IS} \gg \text{DS}$ for the majority of isotopes in most cases, and the latter shift should be taken into account only at high temperatures. ^{67}Zn Mössbauer spectroscopy is among those rare cases where the IS and DS values are of the same order of magnitude and even relation $\text{IS} < \text{DS}$ is possible. This is attributable to the facts that a ^{67}Zn atom has a relatively low mass, the resonance transition has a high energy, and the spectral line is extremely narrow.

Thus, the DS value needs to be taken into account in order to determine the isomeric shift of ^{67}Zn Mössbauer spectra, which contains key information on the electronic

structure of zinc centers. This limits the practical applicability of ^{67}Zn MS in solid-state physics, since DS calculations require integrating over the vibrational spectrum of a Zn probe. Since attempts at applying model vibrational spectra (e.g., Debye model) in theoretical DS calculations were unsuccessful [3], the authors of [1], where ^{67}Zn MS studies of zinc fluoride, oxides, and chalcogenides were performed, calculated the DS values for each compound using complex lattice dynamics models. However, this approach is hardly suitable for routine interpretation of spectra. In addition, such calculations are necessarily made even more complex in the case of impurity probe atoms.

In the present study, a Mössbauer examination of impurity ^{67}Zn atoms in crystal lattices of sodium (NaHal) and cuprous copper (CuHal) halides, where Hal = F, Cl, Br, or I, was performed for the purpose of determining central, isomeric, and Doppler shifts of ^{67}Zn Mössbauer spectra. The possibility of calculation of the quadrupole interaction constant for impurity ^{67}Zn centers in sodium halides within the ionic point-charge model was also demonstrated.

Mössbauer sources were prepared by diffusion doping of ^{67}Cu into either NaCl, NaBr, and NaI single crystals or NaF, CuCl, CuBr, and CuI pellets pressed from powders. A solution of carrier-free (i.e., free of stable copper isotopes) $^{67}\text{CuCl}_2$ in 0.1 N HCl was deposited for this purpose onto the surface of a crystal or a pellet, which were then dried and annealed either in an atmosphere of the corresponding halogen (for NaHal) or in vacuum (for CuHal). ^{67}Cu (^{67}Zn) Mössbauer spectra were measured at 4.2 K with a ZnS absorber. Central and isomeric shifts were taken relative to a ZnO absorber with a wurtzite structure at 4.2 K.

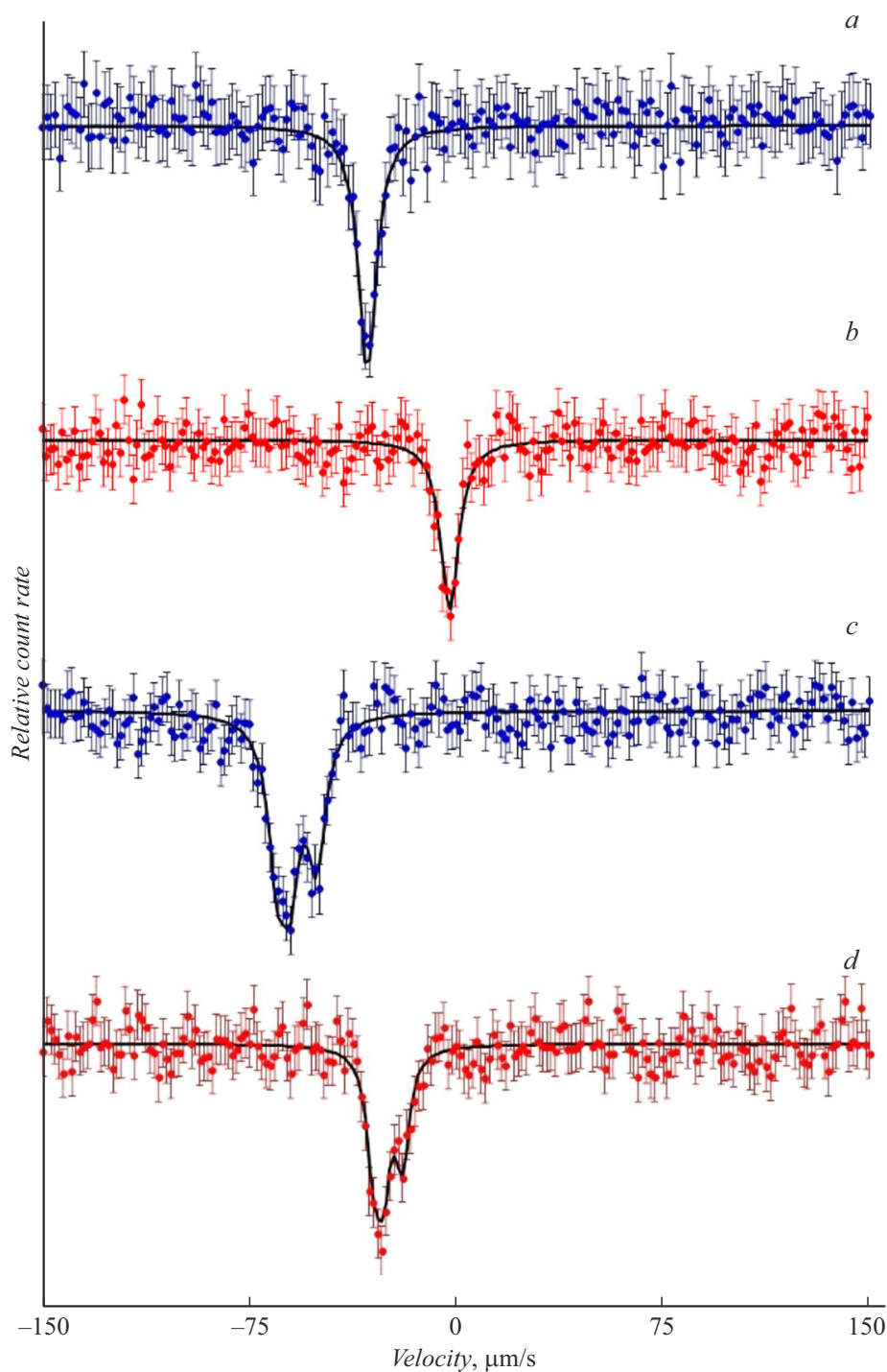


Figure 1. $^{67}\text{Cu}(^{67}\text{Zn})$ emission Mössbauer spectra in sodium and cuprous copper halides relative to a ZnS absorber. The velocity scale is rotated relative to the natural scale in the measurement of emission spectra in such a way that greater transition energies correspond to higher velocities. *a* — CuCl, *b* — CuI, *c* — NaCl, *d* — NaI.

$^{67}\text{Cu}(^{67}\text{Zn})$ spectra of all samples of copper halides are singlet lines corresponding to divalent $^{67}\text{Zn}^{2+}$ (the only possible valence state of zinc) centers, while $^{67}\text{Cu}(^{67}\text{Zn})$ spectra of all samples of sodium halides doped with ^{67}Cu are quadrupole triplets corresponding to divalent $^{67}\text{Zn}^{2+}$ zinc centers (Fig. 1). The asymmetry parameter of all triplets was near-zero ($\eta_{exp} < 0.1$).

The lack of quadrupole splitting of ^{67}Zn spectra for copper halides is due to the tetrahedral environment of zinc centers that are produced at cation sites after the β -decay of monovalent tetrahedrally coordinated parent $^{67}\text{Cu}^+$ atoms. The process of annealing of copper-doped NaHal samples in an atmosphere of halogen vapor stabilizes parent ^{67}Cu at cation sites in the divalent six-coordinated form, while

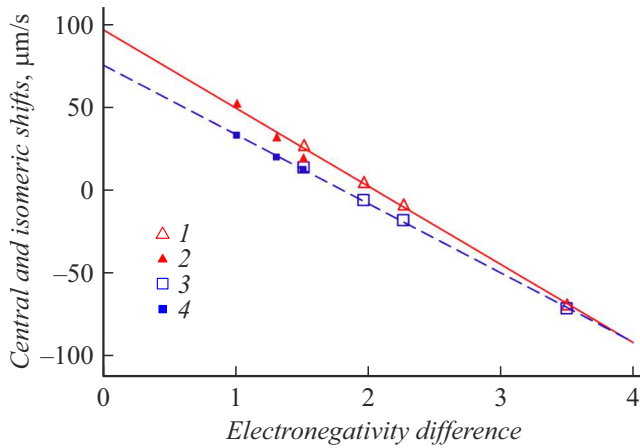


Figure 2. Dependences of CS (1, 2) and IS (3, 4) taken relative to ZnO (wurtzite) on the difference of electronegativities of atoms for sodium (1, 3) and copper (2, 4) halides.

the excess charge of $^{67}\text{Cu}^{2+}$ ions is compensated by cation vacancies that form associates with Cu^{2+} centers. This translates into a lower local symmetry of $^{67}\text{Zn}^{2+}$ centers and induces quadrupole splitting of spectra.

The dependence of the central shift of $^{67}\text{Cu}(^{67}\text{Zn})$ spectra for sodium and copper halides on difference Δx between Pauling electronegativities of zinc atoms and ligand atoms is shown in Fig. 2 (this difference for octahedrally coordinated zinc centers is multiplied by a factor of 1.5 to account for the greater number of nearest neighbors of a zinc atom).

Empirical dependences $\text{DS} = f(\Delta x)$ for four- and six-coordinated zinc centers were used instead of calculations to determine the relativistic DS values. These dependences were derived from the data on DS and Δx for zinc fluoride, oxides, and chalcogenides [1]. Inserting the DS values obtained this way into relation (1), one may determine isomeric shifts of Mössbauer spectra of impurity ^{67}Zn atoms in sodium and copper halides. Such IS estimates are not very accurate, since the error of calculated DS values indicated in [1] is $\pm 8 \mu\text{m/s}$; however, they reveal the trends of IS variation. Figure 2 presents the $\text{IS} = f(\Delta x)$ dependence that is indicative of a linear correlation between isomeric shifts of Mössbauer spectra of impurity ^{67}Zn atoms at octa- and tetrahedral sites in crystal lattices of sodium and copper halides and the ionicity of chemical bonds of zinc and chalcogen atoms.

The spatial localization of a cation vacancy in the local environment of a $^{67}\text{Zn}^{2+}$ center may be established by comparing the experimental parameters of nuclear quadrupole interaction (NQI), which are determined by ^{67}Zn MS, and the parameters of the electric field gradient (EFG) tensor, which are calculated within the point-charge model. Quadrupole interaction constant $C_{exp} = eQU_{zz}$ (eQ is the quadrupole moment of a probe nucleus) and asymmetry parameter η_{exp} are the NQI parameters, and principal component U_{zz} and asymmetry parameter $\eta = (U_{xx} - U_{yy})/U_{zz}$ are the parameters of the diagonalized

EFG tensor for $^{67}\text{Zn}^{2+}$ probe nuclei in a crystal lattice. EFG tensor components U_{xx} , U_{yy} , and U_{zz} are bound by relations $U_{xx} + U_{yy} + U_{zz} = 0$ and $|U_{xx}| \leq |U_{yy}| \leq |U_{zz}|$; in the general case,

$$eQU_{zz} = eQ(1 - \gamma)V_{zz} + eQ(1 - R)W_{zz},$$

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

where V_{zz} , W_{zz} , and U_{zz} are the principal components of lattice, valence, and total EFG tensors; $\eta_{lat} = (V_x - V_{yy})/V_{zz}$ and $\eta_{val} = (W_{xx} - W_{yy})/W_{zz}$ are the asymmetry parameters of lattice and valence EFG tensors; and γ and R are the Sternheimer factors that introduce a correction for anti-shielding and shielding, respectively, of an EFG, which is produced by external charges, by inner electron shells of a probe atom.

Probes with a completely filled (or a half-filled) valence shell have $W_{zz} \approx 0$, and the lattice EFG tensor may be calculated within the point-charge model. Since a regular NaCl-type lattice does not induce an EFG at its sites, a cation vacancy in the nearest-neighbor environment of a $^{67}\text{Zn}^{2+}$ was assumed to be the sole EFG source. The principal component of the lattice EFG tensor for zinc nuclei was calculated as $V_{zz} = 2e^*/r^3$, where r is the Zn–vacancy distance, which is equal to $r_1 = a/2^{1/2}$ or $r_2 = a$ for the first and second coordination shells, respectively, and a is the lattice constant. Vacancy charge e^* was assumed to be negative and equal in magnitude to the charge of an electron. In accordance with the experimental spectra, the EFG tensor asymmetry parameter was set to zero (due to the axial symmetry of the EFG tensor). Experimental values of the quadrupole interaction constant were then compared to lattice EFG contribution $C = \alpha V_{zz}$, where $\alpha = eQ(1 - \gamma)$. Figure 3 shows calculated dependences $C = f(V_{zz})$ for Zn^{2+} centers in NaHal and experimental C values.

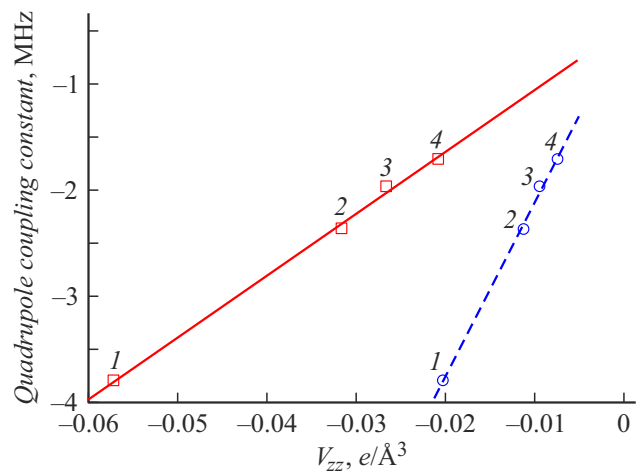


Figure 3. Dependences of the quadrupole interaction constant on principal component V_{zz} of the lattice EFG tensor for impurity ^{67}Zn atoms in NaF (1), NaCl (2), NaBr (3), and NaI (4). Squares and circles correspond to vacancies in the first and second coordination shells, respectively.

Since both dependences are linear, their angular coefficients α may be determined. The value of $\alpha = 58.2 \pm 0.5 \text{ MHz} \cdot \text{\AA}^{-3}/e$ corresponds to a vacancy in the first coordination shell. If the Sternheimer factor is assumed to be $\gamma = -12.2$ [2], the quadrupole moment of a ^{67}Zn nucleus is $Q = 0.13(2)b$, which agrees with the data from [4,5]. Coefficient $\alpha = 164.7 \pm 1.4 \text{ MHz} \cdot \text{\AA}^{-3}/e$ for a vacancy in the second coordination shell yields $Q = 0.37b$, which differs radically from conventional values. Apparently, the difference in electrostatic energies $e^2/4\pi\epsilon_0 r$ in a Zn–vacancy pair, which assumes a value of 1–1.5 eV for r_1 and r_2 (or 0.16–0.25 eV, if an allowance for the medium polarization is made using static permittivity), turns out to be sufficient for vacancy capture in the process of annealing to a minimum distance from the Zn center.

Thus, isomeric shifts of emission Mössbauer spectra of impurity $^{67}\text{Cu}(^{67}\text{Zn})$ atoms in sodium and copper halides were determined, and their correspondence to the nature of chemical bonding between zinc atoms and halogen atoms in the studied crystals was demonstrated. The comparison of experimental and calculated values of quadrupole interaction constants for impurity zinc centers in sodium halides revealed an agreement between them and suggested that a vacancy forming as a result of substitution of alkali metal ions with zinc centers is positioned in the first coordination sphere of alkali metal atoms.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] D.W. Mitchell, T.P. Das, W. Potzel, G.M. Kalvius, H. Karzel, W. Schiessl, M. Steiner, M. Köfferlein, *Phys. Rev. B*, **48** (22), 1649 (1993). DOI: 10.1103/physrevb.48.16449
- [2] E.I. Terukov, A.V. Marchenko, P.P. Seregin, V.S. Kiselev, K.B. Shakhovich, *Phys. Solid State*, **60** (10), 1908 (2018). DOI: 10.1134/S106378341810027X.
- [3] A. Forster, W. Potzel, G.M. Kalvius, *Z. Phys.*, **37** (3), 209 (1980). DOI: 10.1007/BF01323034
- [4] P. Pyykkö, *Mol. Phys.*, **106** (16-18), 1965 (2008). DOI: 10.1080/00268970802018367
- [5] J. Bieroń, L. Filippin, G. Gaigalas, M. Godefroid, P. Jönsson, P. Pyykkö, *Phys. Rev. A*, **97** (6), 062505 (2018). DOI: 10.1103/PhysRevA.97.062505

Translated by D.Safin