Physics of the Solid State, 2024, Vol. 66, No. 1

04,08

Mössbauer study of zinc impurity atoms in alkali metal and copper halides

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Received October 17, 2023
Revised October 17, 2023
Accepted October 24, 2023

The central, relativistic Doppler and isomeric shifts of the emission Mössbauer spectra of ^{67}Cu(^{67}Zn) impurity atoms in the crystal lattices of sodium, potassium, rubidium and monovalent copper halides have been determined. A change in the electronic structure of impurity zinc atoms is demonstrated depending on the chemical nature of the atoms of the immediate environment and their coordination. Based on the comparison of experimental and calculated values of the quadrupole interaction constants for zinc impurity centers in alkali metal halides, it was concluded that the vacancy resulting from the substitution of alkali metal ions by zinc centers is located in the first coordination sphere of the cation sublattice.

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

DOI: 10.61011/PSS.2024.01.57853.229

1. Introduction

One of the benefits of the Mössbauer spectroscopy (MS) is the capability to find the valence and coordination state of a probe atom and the symmetry of its immediate environment according to the isomer shift (IS) and quadrupolar splitting (QS) of the spectrum in a single experiment and even using a single spectrum. In this respect, ^{67}Zn isotope with an isometric transition energy of 93.3 keV is of special interest. First, it has the lowest natural spectral line width ($0.32\,\mu$m/s) among all other isotopes, which corresponds to $\approx 10^{-10}$ eV. Second, high spin of its ground state ($I = 5/2$) provides full information from the experimental spectrum about the nuclear quadrupole interaction tensor [1].

The first Mössbauer spectrum ^{67}Zn was obtained by de Waard and Perlow [2] as early as in 1970. However, there were relatively few further MS applications on ^{67}Zn which covered a small range of materials. This is due, on the one hand, to high transition energy and short lifetimes of ^{67}Ga and ^{67}Cu parent isotopes for the sources, and on the other hand, to the absence of a standard interpretation practice for shifts and splitting of the obtained spectra.

Only a central shift CS is determined directly from the experimental Mössbauer spectrum. This is a sum of the isomer shift IS, that is proportional to the electron density on the nucleus, and of the second-order Doppler shift DS, that is associated with the oscillatory motion of the probe atom

$$CS = IS + DS. \tag{1}$$

It was demonstrated for the majority of isotopes that usually $IS \gg DS$ and the latter shift should be taken into account only at high temperatures. MS on ^{67}Zn is one of rare cases when IS and DS are of the same magnitude. Therefore, to define the isomer shift IS of the Mössbauer spectra that contains the main information on the electronic structure of the zinc centers, DS shall be taken into account.

Griesinger et al [3] measured the Mössbauer spectra of ^{67}Ga sources in ZnO, ZnS, ZnSe and ZnTe crystals with ^{67}ZnO absorber. Linear dependence between the central shifts CS and ratio of the mean atomic weight to the density of the matrix was found. Forster et al [4] studied the same compounds and ZnF_2 as absorbers with ^{67}Ga:Cu source. The obtained central shifts corresponded to the data in [3], but the attempt to isolate the isomer shift using the allowances for DS calculated using the Debye model was not satisfactory. For the interpretation of findings of [4], Mitchell et al [5] performed self-consistency cluster calculations of the second-order Doppler shifts. As a result, it has been shown that for the specified compounds, a linear correlation between the isomer shifts and electron density variations. Later, Köfferlein et al [6] used various lattice behavior models to calculate the second-order Doppler shifts for ^{67}Zn in ZnF_2, ZnO and zinc chalcogenides. Zwanziger [7] calculated the electron densities and *DS* of these compounds by he density functional method and confirmed the presence of the linear dependence, but the resulting values of *DS* differed considerably from the data in [5]. Calculations of *DS* for chalcogenides and zinc oxide were made in a quite large number of papers, however, their results were contradictory, for example, [5] and [7]. Similar calculations of *DS* for chalcogenides and zinc oxide were made in a quite large number of papers (all of them are discussed in [8]), however, their results were contradictory.

It should be noted that calculation of *DS* for ^{67}Zn in [5–8] required complex and cumbersome calculations for each crystal separately. Appropriate calculations shall require much more sophistication for probe impurity atoms. Such way maybe hardly used for routine spectra interpretation and a search for new approaches is required to assess *DS*.

Quadrupolar splitting values for the Mössbauer spectra of $^{67}ZnF_2$ were analyzed by Potzel and Kalvius [9] who found that, though Zn-F bond is regarded as highly ionic, the calculated values of the electric field gradient (EFG) tensor parameters within a simple point charge model do not describe their experimental values for ZnF_2. Later, Steiner et al [8] demonstrated that experimental Mössbauer spectra parameters of $^{67}ZnF_2$ agree well with the theoretical quantum cluster calculations. On the other hand, for the Mössbauer spectra of ^{67}Ga:ZnO [2] and ^{67}Cu:AgCl [10], experimentally determined values of the main component U_{zz} of the EFG tensor in the zinc sites are in good agreement with the calculated U_{zz} in the point charge model. Thus, no there is no common view on the applicability of various methods to calculate the EFG tensor parameters for ^{67}Zn.

A small number of materials investigated using MS on ^{67}Zn (except for the compounds listed above [3,4,10], these are metallic zinc [11] and zinc-manganese alloys [12]. Most of these investigations were performed using ^{67}Ga parent isotope with the last relevant experimental study dated as of 2005 [13]. Investigations of high-temperature superconductors that used ^{67}Cu parent isotope are of some exception [1].

The objective of the study is to investigate the impurity zinc atoms incrystal lattices of alkali metal halogenides and univalent copper by the emission MS method on ^{67}Zn with ^{67}Cu parent isotope, which widens the range of Mössbauer spectroscopy objects. The second objective is to examine whether the empiric methods of data acquisition about central, isomer and Doppler shifts of ^{67}Zn spectra and on the interpretation of quadrupolar splitting or impurity ^{67}Zn centers in the materials of interest. Preliminary findings are published in [14].

2. Experimental procedure

Sodium, potassium and rubidium fluorines, chlorides, bromides and iodides (NaHal, KHal, RbHal) having a rock salt type cubic lattice as well as univalent copper bromides and iodides (CuHal) with a sphalerite type lattice were used as the objects of investigations.

The Mössbauer sources were prepared by ^{67}Cu diffusion either into single-crystal NaCl, NaBr and NaI samples or into pressed-powder tablets for other compounds. For this, solution of carrier-free $^{57}CuCl_2$ in 0.1 H hydrochloric acid was applied to the crystal or tablet surfaces, then they were dried and annealed for 1 h either in the appropriate halogen atmosphere (for alkali metal halides) or in vacuum (for copper halides) at temperatures below the melting temperatures of the appropriate substance by 50°C. Emission Mössbauer spectra of ^{67}Cu(^{67}Zn) were recorded at 4.2 K with ZnS absorber. Values of *CS* and of *IS* derived from them are listed below relative to the most often used ZnO standard in wurtzite modification (*CS* of ZnS absorber relative to ZnO was assumed equal to 54.2 μm/s).

3. Experimental findings and discussion

^{67}Cu(^{67}Zn) spectra of all copper halide samples (Figure 1) singlet lines corresponding to $^{67}Zn^{2+}$centers (the only possible zinc valence state, except for metallic state). ^{67}Cu(^{67}Zn) spectra of all ^{67}Cu-doped alkali metal halide samples represent quadrupole triplets corresponding also to $^{67}Zn^{2+}$ centers. Figure 2 shows only a part of these spectra.

Spectrum width at half maximum of halides is from 6 to 8 μm/s, this is the instrument width of the spectrometer, it is 20–25 times greater than the natural width. Experimental

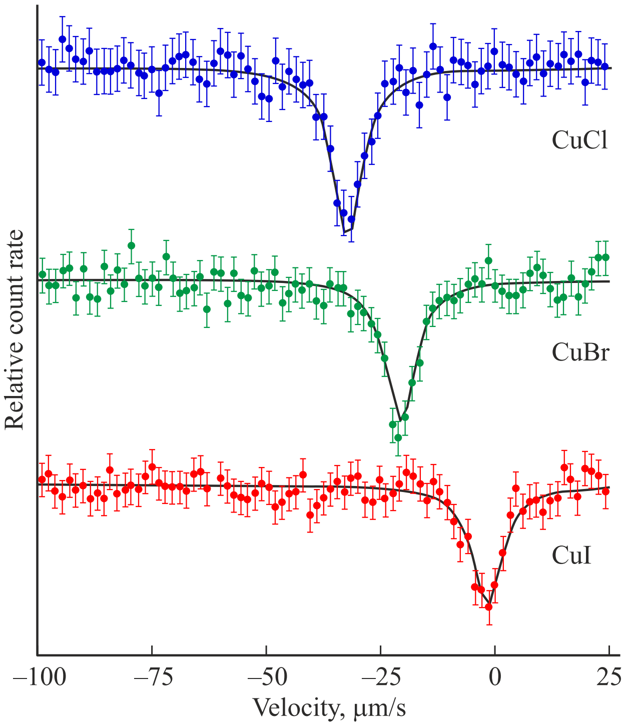

Figure 1. The Mössbauer spectra of monovalent copper halides ^{67}Cu(^{67}Zn) measured with ZnS absorber.

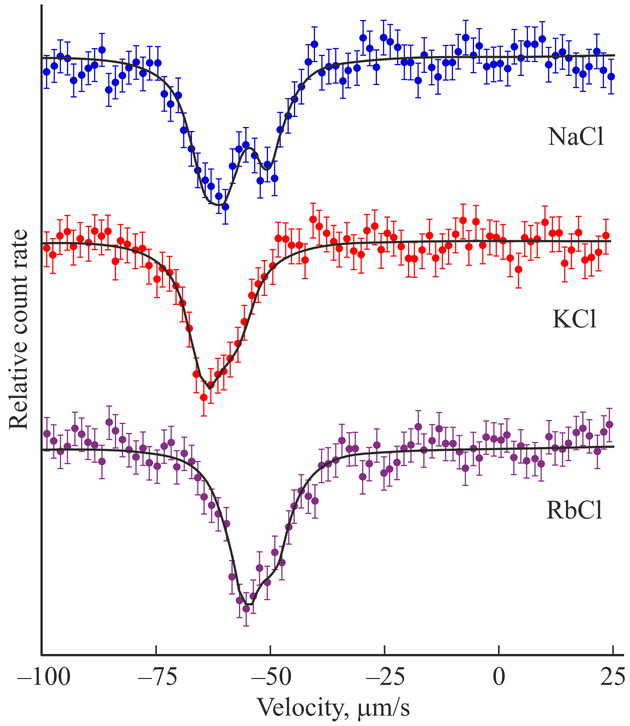

Figure 2. The Mössbauer spectra of ^{67}Cu(^{67}Zn) impurity atoms in alkali metal chlorides measured with ^{67}ZnS absorber.

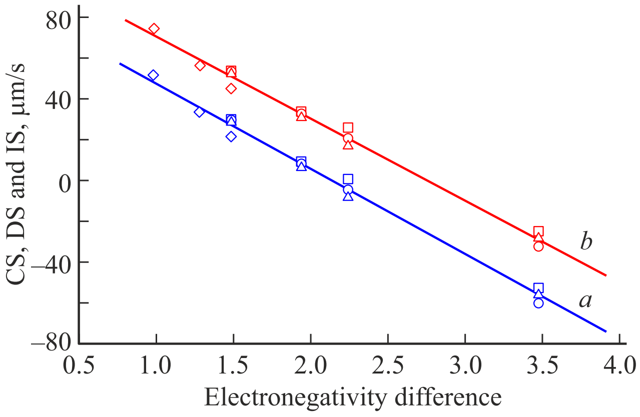

Figure 3. Dependences of central (a), Doppler (b) and isomer (c) shifts of the Mössbauer spectra ^{67}Cu(^{67}Zn) in monovalent copper and alkali metal halides on Pauling's atom electronegativity difference of Zn atoms and ligands.

values of central shifts of CS are within the range from -60 to $+55\,\mu$m/s.

To measure IS, DS shall be validly assessed. Since the theoretical calculations of DS give contradicting results [5–8], in [14], we offered to assess the Doppler shifts DS using empirical correlations between DS of ^{67}Zn impurity atoms in copper and sodium halides and Pauling's electronegativity difference $\Delta\chi$ of Zn atoms and ligands calculated in [5] for ZnF_2, ZnO and zinc chalcogenides using lattice-dynamic calculations. Therefore, experimental data for CS of the materials examined by us are shown in Figure 3, a in the form of dependence $CS = f(\Delta\chi)$. For zinc centers with octahedral coordination in alkali-halide crystals, difference $\Delta\chi$ was multiplied by a coefficient of 3/2 to consider a larger number of the nearest zinc atom neighbors.

Then, we used newer calculations of DS for ZnF_2, ZnO and zinc chalcogenides conducted by Zwanziger [7] and represented them as a linear function of the electronegativity difference of Zn atoms and ligands.

$$DS = -1.9 \times \Delta\chi - 20.3, \qquad (2)$$

where DS in μm/s.

Dependence (2) was used to assess DS for the materials used by us. Absolute values of the Doppler shift happened to vary in the range from 22 to $27\,\mu$m/s, which is comparable with the CSvariation range for ^{67}Zn for different AHC and particularly for different copper halides.

Dependence of the isomer shift values calculated according to $IS = CS - DS$ as a function of $\Delta\chi$ is shown in Figure 3 (curve b). It is described as follows:

$$IS = \mu \times \Delta\chi + \beta = -40.6 \times \Delta\chi + 113.1. \qquad (3)$$

Values of IS are within the range from -30 to $+75\,\mu$m/s. Moreover, low values of $\Delta\chi$ in Figure 3 (curve b) belong to copper halides with tetrahedral coordination. Therefore, extrapolation of $\Delta\chi$ to zero shall result in „pure“ homeopolar bond with two electrons distributed on foursp^3-orbitals of Zn atom (such atom is denoted as $Zn_{\text{homeopolar}}$), and a free term β in expression (3) equal to $113\,\mu$m/s corresponds to the isomer shift $IS_{\text{homeopolar}}$ of this hypothetical atom $Zn_{\text{homeopolar}}$. The second summand $\mu \times \Delta\chi$ in expression (3) is proportional to the deviations of electron density $\Delta\rho(0)$ on Zn nucleus and number $4s$ of zinc atom electrons n_{4s} from those in $Zn_{\text{homeopolar}}$ atom. To find $\rho(0)$ and n_{4s}, it should be considered that, according to the data in [7], dependence of the valence electron density on ^{67}Zn $\rho(0)$ nucleus on $\Delta\chi$ is linear. Its extrapolation to $\Delta\chi = 0$ gives $\rho(0)_{\text{homeopolar}} = 7.83e/a_o^3$, where a_o is the Bohr radius. It corresponds to 1/2 electron on $4s$-shell of Zn atom. The coefficient of proportionality between the electron density $\rho(0)$ and isomer shift IS of ^{67}Zn atom according to [7] is equal to

$$k = \Delta\rho(0)/\Delta IS = 2.62 \cdot 10^{-2}(e/a_o^3)/(\mu\text{m/s}).$$

Therefore, electron densities $\rho(0)$ and number of$4s$ electrons n_{4s} are calculated using the following expressions

$$\rho(0) = \rho(0)_{\text{homeopolar}} + k(IS - \beta), \qquad (4)$$

$$n_{4s} = (n_{4s})_{\text{homeopolar}} + k(IS - \beta)/IS_{\text{homeopolar}}$$

$$= 1/2 - 1/2k(IS - \beta)/IS. \qquad (5)$$

Calculated values of n_{4s} vary from 0.43 to 0.39 in copper halides with tetrahedral bonds and from 0.40 to 0.26 in AHC with octahedral bonds. They are significantly lower than $n_{4s} = 2$ for a free zinc atom and indicate a larger bond

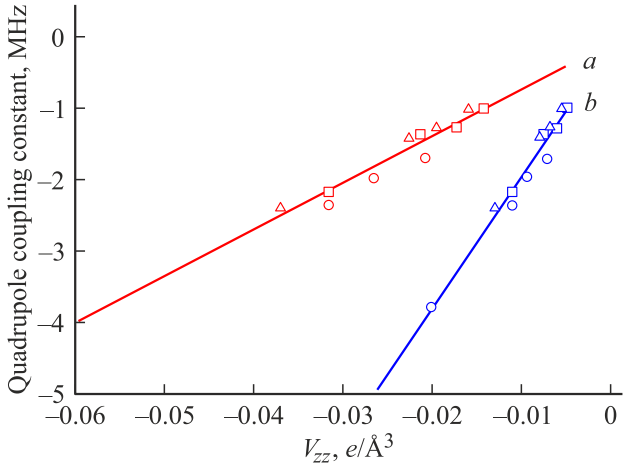

Figure 4. Dependences of the quadrupolar splitting constant on the main tensor component of lattice EFG calculated for the cases of cation vacancies in the first (*a*) and second (*b*) coordination spheres from $^{67}Zn^{2+}$ impurity center.

ionicity fracture of Zn impurity atoms in the compounds of interest. For comparison, n_{4s} for limiting ionic compound ZnF_2 calculated using (5) is equal to 0.21. Inside each group of substances, n_{4s} variations for Zn impurity center are defined by the type halogen in its vicinity. For AHC, n_{4s} variations with changed cation and fixed halogen were < 0.01.

EFG tensor asymmetry parameter determined from the AHC spectra is close to zero, while the quadrupole interaction constants are within the range from -4.8 to -1.0 MHz (see Figure 4).

As shown in [10], if Zn impurity atoms were in the regular AHC lattice sites with cubic symmetry, no quadrupolar splitting shall have been observed. Environment symmetry is broken in sample annealing during ^{67}Cu-doping process. In addition, ^{67}Cu parent atoms in the form of $^{67}Cu^{2+}$ are fixed in the cation positions with halogen ions in the octahedral environment. Excess charge of $^{67}Cu^{2+}$ is compensated by cation vacancies that form associates with Cu^{2+} centers. $^{67}Zn^{2+}$ daughter ion inherits this configuration with a lower local symmetry of centers resulting in the occurrence of the quadrupolar splitting spectrum.

Cation vacancy position in the local environment of $^{67}Zn^{2+}$ center may be found by comparing the experimental parameters of nuclear quadrupole interaction which are determined by MS methods on ^{67}Zn, and the EFG tensor parameters calculated within the point-charge model. The experimental parameters include the quadrupole interaction constant $C_{\text{exp}} = eQU_{zz}$ (here eQ is the quadrupole moment of the probe nucleus) and the spectrum asymmetry parameter η_{exp}. As shown above, η_{exp} is close to 0 in all cases. The appropriate design quantities include the main component of the EFG tensor on $^{67}Zn^{2+}$ U_{zz} probe nuclei and the asymmetry parameter $\eta = (U_{xx} - U_{yy})/U_{zz}$ where diagonal components of the EFG tensor U_{xx}, U_{yy}, U_{zz} are bound by relations $U_{xx} + U_{yy} + U_{zz} = 0$ and $|U_{xx}| \le |U_{yy}| \le |U_{zz}|$. the are generally defined by the contributions of the surrounding ions of the crystal lattice and of the probe atom valence electrons.

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

$$\eta = (1/U_{zz})[(1-\gamma)V_{zz}\eta_{\text{lat}} + (1-R)W_{zz}\eta_{\text{val}}], \qquad (6)$$

where V_{zz}, W_{zz} and U_{zz} are the main tensor components of lattice, valence and total EFG; $\eta_{\text{lat}} = (V_x - V_{yy})/V_{zz}$ and $\eta_{\text{val}} = (W_{xx} - W_{yy})/W_{zz}$ are the tensor asymmetry parameters of lattice and valence EFG; γ and R are the Sternheimer factors that consider anti-shielding and shieldinginner electron shells of the EFG probe atom generated by external charges.

For probes with a completely filled (or a half-filled) valence shell $W_{zz} \approx 0$, and the lattice EFG tensor may be calculated within the point-charge model. Then, the measured C_{exp} and η_{exp} shall be compared with the calculated η_{lat} and $C_{\text{lat}} = eQ(1-\gamma)V_{zz} = \alpha \times V_{zz}$. V_{zz} for zinc centers in cation sites of the AHC crystal lattices was calculated using equation $V_{zz} = 2e^*/r^3$, where r is the Zn-vacancy distance, and the vacancy charge e^* was considered negative and equal to the electron charge in he absolute value. Figure 4 shows dependences $C = f(V_{zz})$ for Zn^{2+} centers in the AHC lattices for two models — the cation vacancy is in the first coordination sphere from the zinc center ($r_1 = a/2^{1/2}$, dependence 1) (model 1) or in the second one ($r_2 = a$, dependence 2) (model 2), where a is the lattice constant in both cases. These dependences are linear and, therefore, coefficient α may be defined for both models: $\alpha_1 = 57(3)\,\text{MHz}\cdot\text{Å}^3/\text{e}$ for model (1) and $\alpha_2 = 162(5)\,\text{MHz}\cdot\text{Å}^3/\text{e}$ for model (2). If the Sternheimer factor of Zn^{2+} is assumed as $\gamma = -12.2$ [15], for the quadrupole moment of ^{67}Zn nucleus, $Q = 0.122(15)b$ [16], and V_{zz} is expressed in e/Å^3, then the expected design value is $\alpha = 56(6)\,\text{MHz}\cdot\text{Å}^3/\text{e}$. It is in satisfactory agreement with the experimental value of α obtained for the model according to which the cation vacancy is in the first coordination sphere of the zinc site. Apparently, the electrostatic energy difference of the Zn — vacancy pair equal to $e^2/4\pi\varepsilon_0 r$ with r_1 and r_2 equal to $1-1.5$ eV, if the medium polarization is considered using static dielectric permittivity) turns out to be sufficient for vacancy capture during annealing to a minimum distance from the Zn center. The free term of the linear dependence $C = f(V_{zz})$ equal to 0.27(5) MHz is low, but is not equal to zero. It corresponds to a low valence contribution to EFG and is likely attributed to non-zero population of the Zn valence shell as found above.

The absence of quadrupolar splitting of ^{67}Zn spectra for copper halides means that Zn impurity atoms are in regular sites of the crystal lattice in a regular tetrahedral environment and, as opposed to the Zn centers in AHC, have no defects in their environment. For this, when $^{67}Cu^{2+}$ parent ions are introduced during annealing, they shall be reduced up to $^{67}Cu^{+}$, for example, due to electron exchange with the matrix ions. $^{67}Zn^{2+}$ centers generated after β-disintegration inherit the $^{67}Cu^{+}$ position in the regular cation sites and cannot change the position during the Mössbauer level lifetime (approximately $9\,\mu$s).

4. Conclusion

Thus, empirical dependences were used to define the second-order Doppler shifts, find isomer shifts of emission Mössbauer spectra of ^{67}Cu(^{67}Zn) impurity atoms in copper and alkali metal halides, and the variation of their electronic configuration was shown depending on the chemical origin and coordination of the immediately surrounding atoms. The comparison of experimental and calculated values of quadrupole interaction constants for zinc impurity centers in sodium halides suggested that a vacancy formed as a result of substitution of alkali metal ions by zinc centers is positioned in the first coordination sphere of the cation sublattice.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by E.Ilinskaya