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The Charge State of Copper Impurity Atoms in AgCl

$^{67}Cu(^{67}Zn)$ emission Mössbauer spectroscopy and measurements of the 64Cu decay rate have shown that copper impurity atoms occupying cation sites of the AgCl lattice are in the Cu+ state when AgCl single crystals are doped with Cu by diffusion in a vacuum. By contrast, diffusion in a Cl2 atmosphere leads to partial transition of copper to the Cu^{2+} state and to association of Cu^{2+} with cation vacancies. The dependence of the copper impurity charge on the ambient atmosphere in annealing of AgCl crystals is explained by the effect of the atmosphere on the concentration of cation vacancies.

Keywords: impurity atoms, electron exchange, Mössbauer emission spectroscopy.

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ЗАРЯДОВОЕ СОСТОЯНИЕ ПРИМЕСНЫХ АТОМОВ МЕДИ В AgCl

Методами эмиссионной мессбауэровской спектроскопии $^{67}Cu(^{67}Zn)$ и измерения скорости радиоактивного распада ^{64}Cu показано, что примесные атомы меди занимают катионные узлы в решетке AgCl и находятся в состоянии Cu^{+}, если кристаллы AgCl легируются медью методом диффузии в вакууме. Диффузия в атмосфере Cl2 приводит к частичному переходу примеси меди в состояние Cu^{2+} и к образованию ассоциатов Cu^{2+} с катионными вакансиями. Зависимость зарядового состояния примеси меди от природы атмосферы отжига кристаллов AgCl объясняется влиянием атмосферы на концентрацию катионных вакансий.

Ключевые слова: примесные атомы, электронный обмен, эмиссионная мессбауэровская спектроскопия.

1. Introduction

Mössbauer spectroscopy is an effective method for investigating the state of impurity atoms in solids [2–7; 11; 12]. Because of the poor solubility of impurity atoms such investigations commonly rely upon the emission variant of Mössbauer spectroscopy (EMS) [8–10]. In EMS, a long-lived radioactive parent isotope is introduced into a sample and decays to give a Mössbauer probe (daughter isotope). In particular, this study employed ^{67}Cu (with a half-life of 59 h) as the parent isotope producing the ^{67}Zn Mössbauer probe upon β-decay (see Fig. 1).

This means that the EMS information is related to the lattice position and environment symmetry of a parent atom and to the charge state of a daughter atom. In some cases (for $^{67}Cu(^{67}Zn)$ impurity atoms in AgCl in the present study), analysis of experimental data allows conclusions to be reached concerning not only the positions and local symmetry of parent impurity atoms but also their charge states.
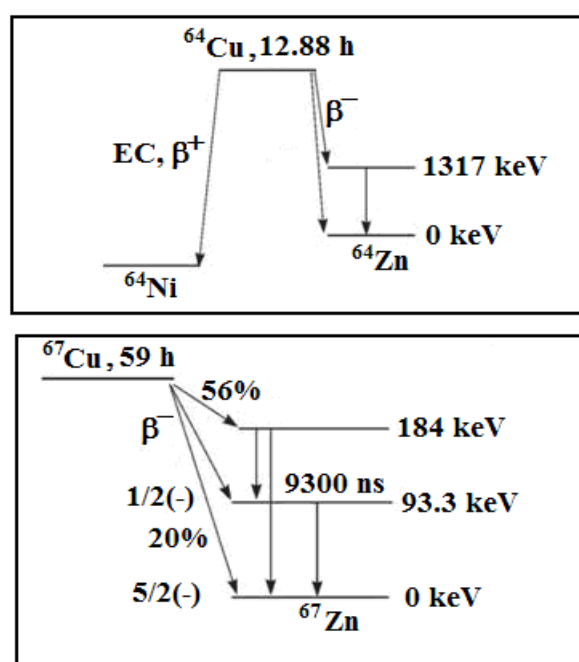
Fig. 1. Schematic representation of radioactive decay of ^{64}Cu *and* ^{67}Cu.

However, independent data are generally required, concerning the charge states of parent atoms. In the present investigation, it is proposed that one can use the dependence of the radioactive decay rate for the ^{64}Cu isotope on the copper valence state [1] as a source of such information.

2. Experimental details

Silver chloride single crystals were grown by the Stock-barger method from optically pure AgCl (the impurity content did not exceed 2×10^{-4} mol.%). Disks of diameter 10 mm and thickness 5 mm with (100) orientation were cut from the grown crystal. The samples were etched in a 10% sodium thiosulfate solution and were annealed at 350 °C for 4 h in an argon atmosphere.

Radioactive AgCl:^{67}Cu and AgCl:^{64}Cu sources were prepared by diffusion of ^{67}Cu or ^{64}Cu into AgCl single crystals. For this purpose, a drop of $^{67}CuCl_2$ or $^{64}CuCl_2$ solution in water was placed on the surface of a crystal, which was then dried and annealed for 1h at 440 °C in a vacuum (AgCl:Cu(I)-type samples) or in an atmosphere of chlorine (AgCl:Cu(II)-type samples). After the annealing, the crystal surfaces were etched in hot hydrochloric acid, washed with ethanol and then etched with a sodium thiosulphate solution. On the basis of Cu diffusion data for AgCl, the average depth of copper diffusion under the above annealing conditions was predicted to be about 0.2 sm.

$^{67}Cu(^{67}Zn)$ Mössbauer spectra were recorded at 4.2 K using an electrodynamic spectrometer with a ZnS absorber having 1000 mg. sm^{-2} surface density in terms of ^{67}Zn.

The decay rate measurements for ^{64}Cu radioactive sources were carried out at room temperature by detecting secondary 511 keV annihilation quanta. A photoelectric multiplier and a 76×76 mm NaI(Tl) crystal with a 40×20 mm well were used in the detector. A source under investigation was placed at the well centre. To check the detector stability, the count rate was measured for two samples alternately with a 240 s period.

3. Experimental results and discussion

Typical Mössbauer spectra of the AgCl:^{67}Cu are shown in Fig. 1, and the results of their processing are summarized in Table.

Parameters of ^{67}Cu(^{67}Zn) Mössbauer spectra and $\Delta\lambda/\lambda$ values for ^{64}Cu (relative to CuCl).
(IS is the isomer shift relative to ZnS, eQU$_{zz}$ is the quadrupole interaction constant,
Q is the quadrupole moment of ^{67}Zn, U$_{zz}$ is the principal component of the electric field
gradient tensor at the ^{67}Zn nuclei, and P is the fraction of singlet I in the total spectrum)

	Spectrum I		Spectrum II			
	IS (μm.s^{-1})	eQU$_{zz}$ (MHz)	IS (μm.s^{-1})	eQU$_{zz}$ (MHz)	P (%)	$(\Delta\lambda/\lambda)\cdot 10^4$
AgCl:Cu(I)	−52.5(5)	< 0.5			100	−0.005(10)
AgCl:Cu(I)	−52.5(5)	< 0.5	−60.0(5)	2.0(3)	15(5)	−1.5(1)
CuCl$_2$						−2.1(1)

The spectrum of an AgCl:Cu(I) sample is a singlet line corresponding to isolated ^{67}Cu impurity atoms (top spectrum in Fig. 2). It will be referred to further as spectrum I. The isomeric shift of spectrum I is typical of Zn^{2+} compounds, and the absence of quadrupole splitting indicates cubic symmetry of the local environment of the copper atoms. Based on conventional notions as to the behavior of copper impurity atoms in AgCl (see, e.g., Ref. 2), spectrum I must be ascribed to ^{67}Zn^{2+} centers formed at regular cation sites of the AgCl lattice after me beta decay of ^{67}Cu.
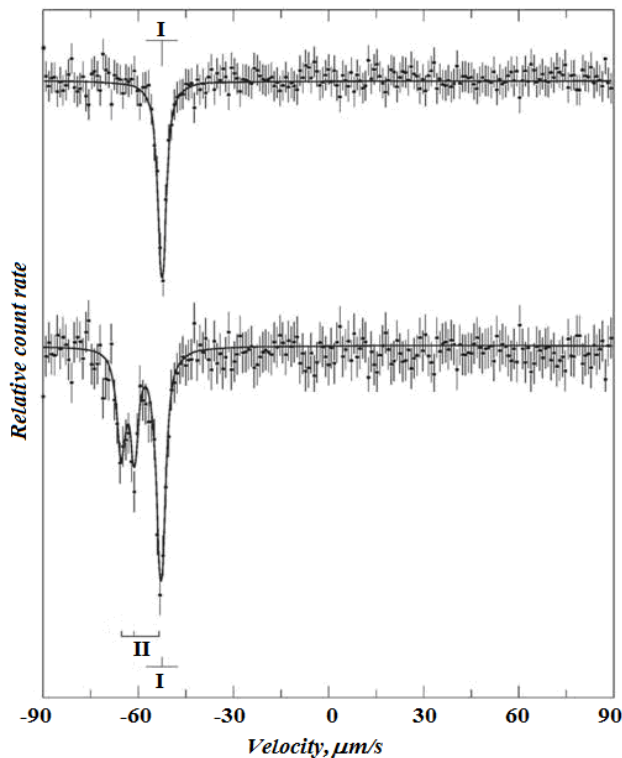

Fig. 2. Mössbauer spectra of ^{67}Cu(^{67}Zn) impurity atoms in AgCl at 4.2 K. The top and bottom spectra correspond to annealing in a vacuum and chlorine, respectively. For the bottom spectrum, the positions of the singlet (spectrum I) and the quadrupole triplet (spectrum II) are indicated. The inset shows the scheme of ^{67}Cu decay

The spectra of AgCl:Cu(II) samples are superpositions of the above singlet (spectrum I) and a quadrupole triplet (spectrum II) (bottom spectra in Fig. 2). The isomer shift of spectrum II corresponds to Zn^{2+}, too. The quadrupole splitting indicates a lowered local symmetry of copper im-

purity atoms. The annealing in chlorine is supposed to stabilize in the Cu^{2+} form a considerable fraction of copper impurity atoms at cation sites of AgCl (see, e.g., Ref. 2). The excess charge of the Cu^{2+} ions is compensated for by cation vacancies forming associations with Cu^{2+}. Thus, spectrum II should be assigned to $^{67}Zn^{2+}$ centres formed in β-decay of $^{67}Cu^{2+}$ at AgCl cation sites, with a cation vacancy in their nearest neighbourhood. This results in a lower local symmetry of the centres and, thus, in a quadrupole splitting of the spectrum.

According to modern concepts, the predominant defects in AgCl are cation vacancies (acceptors) and interstitial Ag^+ ions (donors). Since the copper impurity atoms may be in either of two charge states, Cu^+ and Cu^{2+}, they are donors, too. Annealing in a vacuum ensures electric neutrality of the AgCl lattice by establishing equilibrium between the cation vacancies and the interstitial Ag^+ ions. As a result, impurity copper atoms mainly occupy the normal cation sites in the neutral donor state Cu^+. On the other hand, annealing in chlorine makes the concentration of the cation vacancies higher. The electric neutrality of the lattice requires under these conditions a transition of the copper impurity atoms to the ionized donor state Cu^{2+}, and the mutual attraction of the ionized donors and acceptors must lead to the formation of Cu^{2+}-vacancy associations, which was revealed in the spectra under consideration. Thus, the above spectra are in good agreement with the theoretical predictions concerning the effect of the ambient atmosphere on defect generation in AgCl subjected to thermal treatment.

However, the above interpretation of spectra I and II is based on quite arbitrary assumptions about the charge states of copper impurity atoms and requires some independent experimental verification. This was done by measuring the rate of decay of ^{64}Cu radioactive nuclei. The decay of radioactive nuclei is known to be described by the expression

$$N = N_0 \exp(-\lambda t), \tag{1}$$

where: N and N_0 are the numbers of nuclei at the instant of time t and at the initial instant of time, respectively; $\lambda = \ln 2/T_{1/2}$ is the decay rate; and $T_{1/2}$ is the half-life.

As established experimentally (for ^{64}Cu, see, e.g., [1]), the electron capture (EC) decay rate λ depends on the valence state of decaying atoms. The variations of the decay rate are around 0.01%, and are commonly described by the expression:

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\lambda}{\lambda_1 + \lambda_2}, \tag{2}$$

where $\Delta\lambda = \lambda_1 - \lambda_2$, and λ_1 and λ_2 are the decay rates for the isotope in chemical forms 1 and 2.

There is no reliable theory describing the dependence of $\Delta\lambda/\lambda$ on the chemical parameters of a radioactive compound. However, the key role of the electron density at a decaying nucleus, $|\Psi(0)|^2$, is commonly accepted:

$$\frac{\Delta\lambda}{\lambda} \sim \left[|\Psi(0)_1|^2 - |\Psi(0)_2|^2 \right], \tag{3}$$

where $|\Psi(0)_1|^2$ and $|\Psi(0)_2|^2$ are the electron densities at the radioactive nuclei in compounds 1 and 2, respectively.

The experimental method of determining $\Delta\lambda/\lambda$ consists in measuring the normalized ratio R of the count rates for two sources 1 and 2 as a function of time (the quasi-differential method). This dependence is described by the expression

$$R(t) = \frac{R_1}{R_2} = \exp(\lambda t), \tag{4}$$

where: $R_t = C_1/C_2$, where $C_1(t) = k\lambda_1 N_{01}\exp(-\lambda_1 t)$ and $C_2(t) = k\lambda_2 N_{02}\exp(\lambda_2 t)$ are the count rates for sources 1 and 2, respectively; k is the detector efficiency; N_{01} and N_{02} are the numbers of radioactive nuclei in sources 1 and 2, respectively, at the initial instant of time; and R_0 is the initial ratio of the count rates.

The ^{64}Cu isotope ($T_{1/2}$ = 12.88 h) provides the optimal conditions for $\Delta\lambda/\lambda$ measurements by the quasi-differential method. The ^{64}Cu decay occurs by three channels: EC (43%), β^+ (19%), and β^- (38%), as shown in figure 1. A large body of experimental data concerning the dependence of λ on the chemical state of copper are currently available for this isotope [1].

Fig. 3 shows typical R(t) dependences recorded for the source pairs CuCl-CuCl$_2$, CuCl-AgCl:Cu(I), and CuCl-AgCl:Cu(II). The $\Delta\lambda/\lambda$ values derived from these curves are given in table 1. It can be seen from table 1 and Fig. 3 a that the maximum value of $\Delta\lambda/\lambda$ is observed for CuCl-CuCl$_2$. This fact has an obvious explanation: the above compounds contain copper in two different valence states, Cu$^+$ and Cu^{2+}, with electron configurations $3d^{10}$ and $3d^9$. The transition from $3d^{10}$ to $3d^9$ increases $|\Psi(0)|^2$ and, as a result, increases the rate of decay of ^{64}Cu.
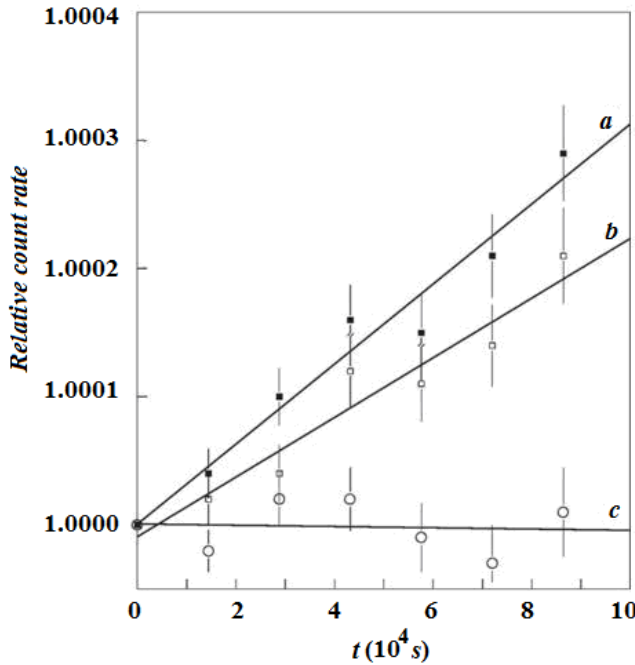

Fig. 3. R(t) dependences for the source pairs CuCl-CuCl$_2$ (a), CuCl-AgCl:Cu(II) (b), and CuCl-AgCl:Cu(I) (c). The inset shows the scheme of ^{64}Cu decay

Comparison with the case for the CuCl-AgCl:Cu(I) source shows that the $\Delta\lambda/\lambda$ value is within the error limits (Fig. 3, c), obviously indicating the Cu$^+$ state of the copper impurity in AgCl doped in a vacuum. By contrast, the $\Delta\lambda/\lambda$ value for the CuCl-AgCl:Cu(II) source is considerably higher (Fig. 3 b), although it is not as large as that for the third pair, CuCl-CuCl$_2$ (see Table 1). In other words, annealing of AgCl in chlorine stabilizes a proportion of the copper atoms in the Cu^{2+} state. With the $\Delta\lambda/\lambda$ value assumed to be proportional to the Cu^{2+} fraction, AgCl:Cu(II) samples must have about 70% of copper in this state, in good agreement with the Mössbauer data.

4. Conclusions

Investigations of diffusion-doped AgCl single crystals by ^{67}Cu(^{67}Zn) emission Mössbauer spectroscopy and measurements of the ^{64}Cu decay rate have shown that copper atoms substitute for silver. However, the charge states of copper proved to be dependent on the doping proportion of the copper into the Cu^{2+} state. The dependence of the charge state of the copper impurity on the ambient atmosphere in the annealing of AgCl crystals is explained by the effect of the ambient atmosphere on the concentration of cation vacancies.

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СВЕРХТОНКИЕ ВЗАИМОДЕЙСТВИЯ В УЗЛАХ МЕДИ РЕШЕТОК ВЫСОКОТЕМПЕРАТУРНЫХ СВЕРХПРОВОДНИКОВ, ИЗУЧЕННЫЕ МЕТОДОМ МЁССБАУЭРОВСКОЙ СПЕКТРОСКОПИИ

Измерены эмиссионные мёссбауэровские спектры $^{61}Cu(^{61}Ni)$ простых оксидов MgO, NiO, Cu_2O, CuO и сверхпроводящих металлооксидов меди $La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO$, $YBa_2Cu_3O_{7-x}$ и $YBa_2Cu_{3-x}Fe_xO_{7+v}$. Показано, что эмиссионная мёссбауэровская спектроскопия на изотопах $^{61}Cu(^{61}Ni)$ позволяет определять параметры тензора градиента электрического и величины магнитных полей поля в медных узлах решеток высокотемпературных сверхпроводников и родственных материалах.

Ключевые слова: мёссбауэровская спектроскопия, высокотемпературные сверхпроводники, сверхтонкие взаимодействия.

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Hyperfine Interactions in Copper Site of Lattices of High Superconductors Studied by Mössbauer Spectroscopy

$^{61}Cu(^{61}Ni)$ Emission Mössbauer spectra of simple oxides MgO, NiO, Cu_2O, CuO and superconducting copper metal oxides $La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO$, $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_{3-x}Fe_xO_{7+v}$ were measured. It is shown that the emission Mössbauer spectroscopy on the $^{61}Cu(^{61}Ni)$ isotopes allows to determine the parameters of the electric field gradient tensor and the value of the magnetic fields in the copper sites of high-temperature superconductor lattices and in the related materials.

Keywords: Mössbauer spectroscopy, high superconductors, hyperfine interactions.

Мёссбауэровская спектроскопия широко используется для изучения сверхтонких взаимодействий в решетках высокотемпературных сверхпроводников (ВТСП) на основе оксидов меди. Особое значение такие исследования имеют, если мёссбауэровский зонд находится в узлах меди. Именно это обстоятельство побудило авторов [1; 5; 9] предложить и реализовать для исследования ВТСП эмиссионную мёссбауэровскую спектроскопию (ЭМС) на изотопах $^{67}Cu(^{67}Zn)$. Мёссбауэровский зонд $^{67}Zn^{2+}$, образующийся после радиоактивного распада материнского изотопа ^{67}Cu, оказывается локализованным в медных узлах решетки, а ядерные и атомные параметры зонда таковы, что позволяют определять тензор градиента электрического поля (ГЭП) в узлах меди, создаваемый ионами кристаллической решетки [2; 12].