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ATOMIC STRUCTURE AND NONELECTRONIC PROPERTIES OF SEMICONDUCTORS

^{63}Cu and ^{115}In NMR Study of $CuInS_2$ Semiconductor

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Abstract—Two $CuInS_2$ semiconductor samples synthesized from chemical elements with the equiatomic cation ratio ($N_{Cu}/N_{In} = 1$) and either an excess or stoichiometric sulfur content have been investigated by ^{63}Cu and ^{115}In nuclear magnetic resonance. The spectra were recorded on a Bruker Avance-400 spectrometer at a temperature of 290 K and frequencies of 106.14 MHz (^{63}Cu) and 87.67 MHz (^{115}In). Numerical simulation made it possible to determine the quadrupole coupling constants: 0.34 MHz (^{63}Cu) and 1.1 MHz (^{115}In). For the samples synthesized with excess sulfur (above stoichiometry), distortions are revealed in both the ^{63}Cu and ^{115}In spectra.

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1. INTRODUCTION

Currently, much attention is being paid to the development of semiconductor solar power engineering (in particular, search for new promising materials) throughout the world. I–III–VI semiconductor compounds ((I) Cu, Ag; (III) Al, Ga, In; (VI) S, Se, Te) with the structure of natural mineral chalcopyrite $CuFeS_2$ form a group of the most promising materials for inexpensive and effective solar cells. The investigations on the application of these compounds for photovoltaic transformation, started in [1], stimulated development of new nanomaterials for 3D solar cells [2]. Among these materials, the $CuInS_2$ (copper indium sulfide) semiconductor has been the most investigated as a basis for *p*-type absorber layers in 3D solar cells. This compound is a direct-gap semiconductor with the band gap $E_g = 1.55$ eV (a value close to the peak solar energy); it has a large optical absorption coefficient ($\alpha > 10^5$ cm^{-1}) and exhibits effective radiative recombination. It was theoretically shown that a solar energy conversion efficiency of 27–35% can be obtained in $CuInS_2$-based *p–n* homojunctions [3]; the experimentally obtained solar energy conversion efficiency in thin-film devices ranges from 11 to 15% [4]. The $CuInS_2$ compound is crystallized into a tetragonal chalcopyrite structure with the lattice parameters $a = (5.5220 \pm 0.0013)$ Å and $c = (11.1320 \pm 0.0023)$Å [5] and a melting temperature of 1363 K [6]. It was shown in [7] that the domain of existence for $CuInS_2$ is very narrow and limited for $Cu_{1-x}In_{1+x}S_2$ by the composition range $0 < x < 0.05$. The electronic structure for this semiconductor is formed with participation of copper atoms, resulting in complex dependences of the optical properties on the qualitative and quantitative composition (primarily, on the cation ratio N_{Cu}/N_{In}, where N_{Cu} and N_{In} are, respectively, the relative fractions of copper and indium in the compound), the degree of atomic ordering in the lattice, and the presence of defects.

An important problem in the studies aimed at increasing the solar cell efficiency is the atomic diffusion in copper indium sulfides. At room temperature, the diffusion coefficient of Cu atoms in $CuInS_2$ is in the range from 10^{-17}–10^{-14} m^2/s. On the whole, $CuInS_2$-based devices have good characteristics; however, it was found that the electric properties of this material change due to the mobility of Cu atoms. Therefore, the effect of copper diffusion on the long-term operation and stability of these devices should be additionally studied. At the same time, additional sulfur atoms cause structural defects, which also play an important role in the electric properties and stabilization of the crystal structure [8]. Previous investigations of these materials at the frequencies of ^{63}Cu and ^{115}In nuclear magnetic resonance (NMR) gave valuable information about the structural and dynamic properties, including the characteristics of the electric quadrupole interactions and diffusion coefficient of Cu(I) at high temperatures [9–11]. At the same time, analysis of the data in the literature has shown a difference in the estimates of the quadrupole coupling constants obtained by different researchers. In this study, we performed ^{63}Cu and ^{115}In NMR analysis of two $CuInS_2$ samples, synthesized from

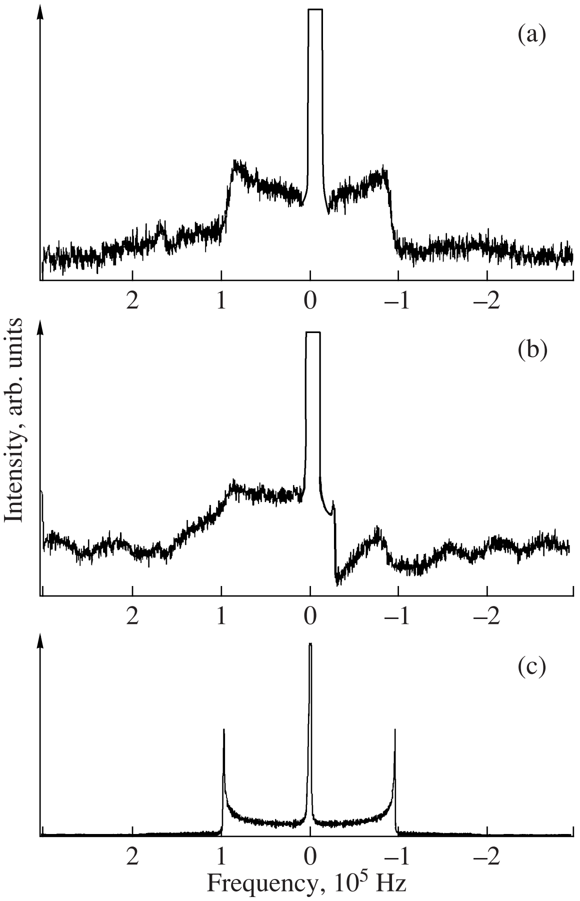

Fig. 1. ^{63}Cu NMR spectra of $CuInS_2$: (a) sample *2*, (b) sample *1*, and (c) the calculation result; $T = 290$ K; the resonant frequency $\nu = 106.14$ MHz.

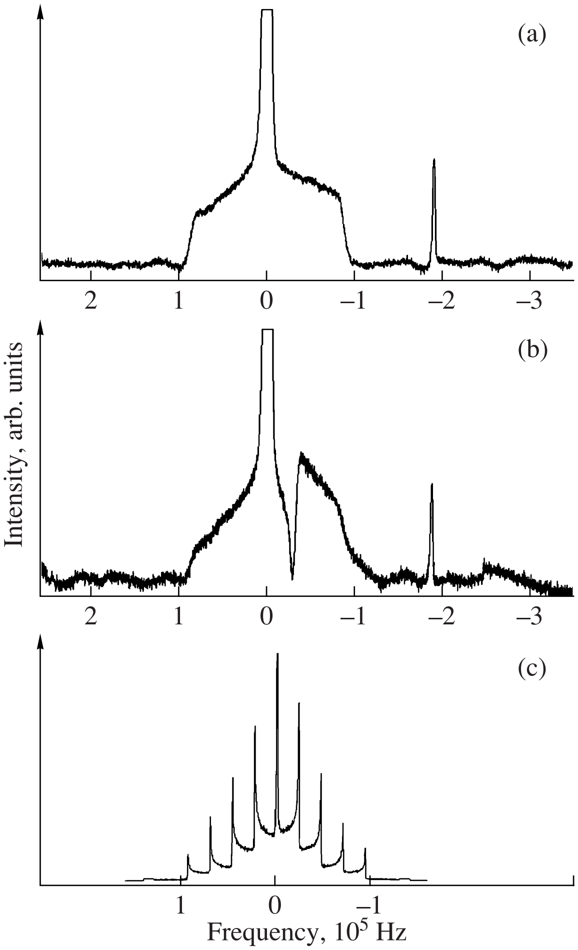

Fig. 2. ^{115}In NMR spectra of $CuInS_2$: (a) sample *2*, (b) sample *1*, and (c) the calculation result; $T = 290$ K and the resonant frequency $\nu = 87.67$ MHz.

chemical elements with an equiatomic cation ratio ($N_{Cu}/N_{In} = 1$) and either sulfur excess with respect to stoichiometry (sample *1*) or a stoichiometric sulfur amount (sample *2*). The sulfur excess was used to eliminate dissociation (decomposition) for the material obtained.

2. EXPERIMENTAL

The NMR analysis was performed on powder samples with characteristic particle sizes of ≤50 μm at $T =$ 290 K using a Bruker Avance-400 spectrometer. Resonant spectra were recorded at the frequencies $\nu =$ 106.14 MHz (^{63}Cu) and 87.67 MHz (^{115}In). The samples were 0.3 cm^3 is volume, and the required signal-to-noise ratio was obtained after collecting 1000–2000 transient processes. To compare the lines for samples of series *1* and *2*, the measurements were performed at the same pulse width for both samples. The spectra were derived by Fourier transformation of the free induction falloff after a 90° pulse with a width of 3 μs. The ^{63}Cu NMR spectrum (spin $I = 3/2$) consists of a central peak, whose shape is determined by the chemical shift anisotropy, and wide satellites due to lateral quadrupole broadened transitions (Fig. 1). The satellites, due to the ($\pm 3/2 \longleftrightarrow \pm 1/2$) transitions arise as a result of first-order quadrupole interactions and lie in a frequency range of 200 kHz. In both samples, the ^{63}Cu central peak has a width of 20 kHz. Due to the finite pulse width, the visible intensity of the central line and lateral satellites is distorted.

The ^{115}In NMR spectrum (spin $I = 9/2$) also consists of a central narrow (12 kHz) peak and quadrupole-broadened lateral transitions with widths of 180 kHz (Fig. 2). The weak peak at approximately 185 kHz at the resonant frequency ($\nu = 87.67$ MHz) is a ^{113}In signal. Analysis of the spectra shows that the central peaks in the ^{63}Cu and ^{115}In spectra for both samples have nearly the same shape; at the same time, their quadrupole-broadened parts are different. It is likely that sulfur atoms are incorporated into the lattice of sample *1*, synthesized at a sulfur excess; as a result, vacancies of metal atoms (Cu, In) are formed in the structure. In sample *2*, the elemental ratio exactly corresponds to stoichiometry. Thus, the technique for sample preparation affects the quadrupole-broadened part of the NMR spectrum but does not change the central peak. The second-order quadrupole broadening of the central transition (observed for the high-temperature line in weaker fields [9]) is much weaker than the contributions of the chemical shift anisotropy and magnetic dipole interactions. Since the spectra exhibit differences only in the satellites, the effects related to the central transition are not considered here.

3. NUMERICAL SIMULATION

Analysis of the quadrupole-broadened part of the spectrum for the single-crystal samples allows one to calculate the quadrupole coupling constant Q_{cc}. To this end, we used the relation

$$\nu_Q = \frac{3e^2qQ}{2I(2I-1)h},$$

where ν_Q is the quadrupole splitting parameter, eq is the principal component of the electric field gradient tensor, and eQ is the nucleus quadrupole moment. The quadrupole coupling constant is defined as

$$Q_{cc} = \frac{e^2qQ}{h}.$$

For ^{63}Cu and ^{115}In nuclei, we have $Q = -0.21 \times 10^{-28}$ and 1.16×10^{-28} m^2, respectively.

The spectra were recorded on powder samples and, therefore, the quadrupole coupling constants could not be directly determined. To this end, we performed numerical simulations for the spectra using the Simpson programs [12]. Figures 1c and 2c show the calculated spectra. It can be seen that the characteristic singularities observed in the calculated spectra are significantly smoother than in the real ones. The reason is that, as was noted above, we analyzed only the quadrupole effects and neglected the broadening caused by the chemical shift anisotropy, as well as the magnetic dipole broadening. Comparison with the data in the literature shows that this approach gives an error of 7%.

The quadrupole coupling constants obtained by fitting are comparable with the known data in the literature for stoichiometric compositions [11, 13, 14]: Q_{cc} = 0.34 and 1.1 MHz for ^{63}Cu and ^{115}In, respectively.

For sample *1*, which was synthesized at a sulfur excess, distortions were observed for both copper and indium resonances against the background of a wide quadrupole-broadened spectrum. This pattern can be explained as follows: incorporation of additional sulfur atoms causes lattice distortion at the sites for metal atoms (specifically, formation of copper and indium vacancies). In this study, we did not investigate the spectral distortion and it was disregarded in numerical simulation; however, it may arise as a result of the filling of indium vacancies by some part of copper atoms and vice versa.

4. CONCLUSIONS

Two CuInS$_2$ semiconductor samples, synthesized from chemical elements with an equiatomic cation ratio (N_{Cu}/N_{In} = 1) and either an excess (with respect to stoichiometry) or a stoichiometric amount of sulfur (samples *1* and *2*, respectively) were investigated by ^{63}Cu and ^{115}In NMR spectroscopy to reveal the influence of structural defects on the Cu(I) and In(III) environment. The ^{63}Cu and ^{115}In NMR lines are broadened by quadrupole interactions, chemical shift anisotropy, and magnetic-dipole interactions. The spectra of the samples synthesized with the sulfur excess exhibit distortions, which indicate sharp changes in the lattice structure. The sulfur excess affects most significantly the quadrupole-broadened part of the spectrum, without changing the central peak, whose shape is determined by the chemical shift anisotropy. Analysis of the NMR spectra allowed us to find the quadrupole-coupling constants: 0.34 MHz for ^{63}Cu and 1.1 MHz for ^{115}In.

To reveal the influence of these changes on the efficiency for CuInS$_2$ as a solar cell material, it is necessary to carry out additional experiments and the corresponding calculations.

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