Research of New Thermoelectric Materials Based on Multicomponent Semiconductor Compounds

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Abstract. This paper presents the results of studies of new thermoelectric materials, obtained on the basis of multicomponent semiconductor compounds with a crystal structure of chalcopyrite and delafossite, by methods of nuclear magnetic resonance in a local field (³¹⁷⁵⁷³Cu NMR) and nuclear quadrupole resonance (⁶³⁶⁵Cu NQR). The values of local magnetic fields at the location of the resonant copper nuclei and the parameters of nuclear quadrupole interactions in chalcopyrite (CuFeS₂) and copper aluminate (CuAlO₂) are determined. The search for new thermoelectric materials is caused by the low operating efficiency of industrial thermoelectric converters based on bismuth and lead tellurides, which have been used for half a century.

1. Introduction

Using thermoelectric phenomena, it is possible to convert thermal energy into electrical energy, carried out in thermoelectric generators (TEG), and thermoelectric cooling, carried out in thermoelectric coolers (TEC) [1]. It should be noted a very important factor from the technical point of view - the indicated energy conversion processes are direct. In addition, solid-state thermoelectric power converters (TPEs) have a number of advantages over traditional electrical devices. These advantages include: high stability of operating parameters, simplicity of design, high reliability, the possibility of miniaturization without loss of efficiency [2,3]. Despite the noted advantages of thermoelectric energy conversion, it has a serious drawback - relatively low efficiency. It is lower than that of conventional electric generators or refrigerators, and therefore TPEs are not widely used in industry. Only a number of applications have emerged where their advantages outweigh their disadvantages: sources of electricity on spacecraft, electrochemical protection of main gas pipelines in hard-to-reach areas, portable refrigeration units, cooling of infrared receivers and optoelectronic devices, etc. For a wide industrial application of thermoelectric energy converters, it is necessary to significantly increase the thermoelectric figure of merit of materials \( Z = \left( \frac{\sigma \alpha^2}{k} \right) \), where \( \sigma \), \( \alpha \), \( k \) are the coefficients of electrical conductivity, thermopower and thermal conductivity. It can be seen from the above formula that a highly efficient thermoelectric material must simultaneously have high electrical conductivity, high thermoelectric power, and low thermal conductivity, but the combination of such properties in semiconductor compounds is a rare phenomenon and the selection of objects for obtaining highly efficient thermoelectric materials is very limited. Recently, interest in the
development of TPEs has noticeably increased and this is largely due to the search for new thermoelectric materials [4, 5]. In this regard, an interesting approach to improving thermoelectric efficiency is the use of magnetic semiconductors [6–9]. The main task in the physics of thermoelectric materials is to simultaneously optimize thermal and electronic properties, and the mechanisms that determine these properties should not compensate each other. Therefore, in order to create materials with high thermoelectric efficiency required for wide practical applications, the main role is assigned to physical research, because, first of all, it is important to understand the microscopic properties of thermoelectric materials. Understanding these properties is a necessary condition for a targeted search for new highly efficient thermoelectric materials.

Among the physical methods for studying materials, modern multi-pulse methods of nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) occupy a special place, since they are one of the most effective methods for studying the electronic structure, defect structure, and dynamic characteristics of thermoelectric materials. This paper presents the results of studies by $^{63,65}$Cu NQR and $^{63,65}$Cu NMR in the local field of thermoelectric compounds belonging to two groups. The first group is represented by samples of a semiconducting mineral - chalcopyrite CuFeS$_2$; the second group includes samples of the semiconductor compound CuAlO$_2$, which has a delafossite crystal structure.

2. Research results

The NMR spectrum of $^{63,65}$Cu in a local field in the studied samples of the CuFeS$_2$ compound should be attributed to resonance signals from nonmagnetic copper ions Cu$^+$. This spectrum was studied in the temperature range 77–300 K [10–12]. It consists of six relatively narrow resonance lines; Such a structure of the spectrum is due to the existence at the location of the resonant nuclei of two common isotopes of copper $^{63}$Cu and $^{65}$Cu of a local magnetic field created by the magnetic moments of iron ions, and the interaction of the quadrupole moments of $^{63}$Cu and $^{65}$Cu nuclei with electric field gradients (EFG) created at the location of the nuclei by their charge surroundings. The NMR spectrum of Cu in a local field for each copper isotope has three resonance lines (the nuclear spin of both isotopes is I = 3/2) and consists of a central line and two quadrupole satellites. The ratios of the resonance frequencies and intensities of the lines detected correspond to the ratios of the nuclear magnetic and quadrupole moments and the natural abundances of these isotopes (the natural abundances of $^{63}$Cu and $^{65}$Cu isotopes are 69% and 31%, respectively). In this case, in the presence of an internal magnetic field, the total nuclear spin Hamiltonian with a quadrupole moment can be represented as:

$$\hat{H} = \hat{H}_m + \hat{H}_q,$$

where $\hat{H}_m$ is the Hamiltonian of the magnetic interaction; $\hat{H}_q$ is the Hamiltonian of the nuclear quadrupole interaction. If $\hat{H}_m \gg \hat{H}_q$, then in the NMR spectra for each copper isotope a triplet with a central line, the frequency of which is determined by the Larmor precession in a local magnetic field and two equidistant satellites for the spin I = 3/2 (in the first approximation of the perturbation theory), will be recorded, which and is observed in the experimental spectrum [11, 12]. The distance between the satellites $\Delta$ allows determining the quadrupole frequency $\nu_Q$ ($\Delta = 2\nu_Q$), the value of which is proportional to the principal component of the EFG tensor $V_{zz}$. The parameters of the Hamiltonian obtained from the experimental $^{63,65}$Cu NMR spectrum at a temperature of T = 77 K are given in Table 1. For both Cu isotopes, the internal magnetic fields $B_{int}$ were calculated from the center line frequency $\nu_{cl}$. The values of the modified GEP $\nu_Q/V$ are also given. The obtained values of $B_{int}$ and $\nu_Q/V$ are determined only by the environment of Cu nuclei and do not depend on the isotope type. It can be seen that these values are indeed equal for both common copper isotopes.
### Table 1. Frequencies of the central line \( v_{cl} \), internal magnetic fields \( B_{int} \) in the positions of copper nuclei, quadrupole frequencies \( v_Q \) and modified EFG \( v_Q/Q \) for \(^{63,65}\text{Cu} \) isotopes.

| Isotopes | \( v_{cl}, \text{MHz} \) | \( B_{int}, \text{T} \) | \( v_Q, \text{MHz} \) | \( v_Q/Q \times 10^{24}, \text{MHz/cm}^2 \) | \( \gamma, \text{MHz/T} \) | \( Q \times 10^{-24}, \text{cm}^2 \) |
|----------|----------------|----------------|----------------|-------------------------------|----------------|----------------|
| \(^{63}\text{Cu} \) | 19.81 | 1.76 | 2.23 | 10.55 | 11.285 | -0.211 |
| \(^{65}\text{Cu} \) | 21.24 | 1.76 | 2.06 | 10.56 | 12.089 | -0.195 |

Each iron or copper atom in chalcopyrite is surrounded by four sulfur atoms, and each sulfur atom is surrounded by two copper atoms and two iron atoms. The layers of iron and copper atoms are separated by layers of sulfur atoms. A slight distortion of the CuS₄ tetrahedron along the crystallographic c axis leads to the appearance of electric field gradients (EFG) at the location of copper nuclei. In the metal layer, iron atoms are ordered ferromagnetically, but adjacent metal layers have oppositely directed spins, so that, on the whole, the crystal is an antiferromagnet (AFM) with a high Néel temperature \( T_N = 823 \text{ K} \). At room temperature, chalcopyrite is in an antiferromagnetic state, with the direction of the magnetization vector along the c axis. Based on the temperature measurements of the magnetic moment and conductivity, it is concluded that chalcopyrite, which is a crystalline semiconductor, manifests itself mainly in a covalent rather than ionic type of bond. In this case, the angle between the direction of the magnetic field and the direction of the main (largest) axis \( V_{zz} \) of the EFG turned out to be very close to 90°.

The second group studied consisted of samples of the semiconductor compound CuAlO₂, which has a delafossite crystal structure. This semiconducting compound belongs to the class of transparent conducting oxides CuMO₂, where M is a trivalent metal (M = Al, Ga, In, Sc, Y, Cr), with p-type conductivity. The active interest shown in these compounds, which have a unique combination of optical and electrical properties, is associated with the possibility of their practical use in various technical devices, including as thermoelectric materials. The \(^{63,65}\text{Cu} \) NQR spectrum in the samples of the semiconductor compound CuAlO₂ at room temperature consists of two lines assigned to the NQR signals from two copper isotopes \(^{63}\text{Cu} \) and \(^{65}\text{Cu} \), with different natural abundances \((^{65}\text{NA} / ^{63}\text{NA} = 0.45)\). The nuclear spins of both copper isotopes are the same \((I = 3/2)\), but the gyromagnetic ratios \( \gamma_N \) and the quadrupole moments Q are different: \( \gamma_N = 7.11 \cdot 10^7 \text{ rad} \cdot \text{s}^{-1} \cdot \text{T}^{-1} \), and \( Q = -22 \cdot 10^{-30} \text{ and } -20.4 \cdot 10^{-30} \text{ m}^2 \) for \(^{63}\text{Cu} \) and \(^{65}\text{Cu} \), respectively. It turned out that the ratio of the resonance frequencies of copper isotopes \( v_Q \) is equal to the ratio of their nuclear quadrupole moments: \( v_Q/^{65}v_Q = Q/Q = 1.08 \). The measured \(^{63,65}\text{Cu} \) NQR spectrum has a structure consisting of two lines and corresponds to a single crystallographic position of copper atoms in the structure of the CuAlO₂ compound, which refers to the crystal structure of the delafossite mineral (CuFeO₂) \([13, 14]\). The obtained values of the parameters of nuclear quadrupole interactions turned out to be equal: \( v_Q = 28.12 \text{ MHz} \), \( \eta \sim 0 \), \( QCC = v_Q = 56.24 \text{ MHz} \). Estimated calculations of the electric field gradients on copper nuclei were made by the ab initio method using the cluster approach based on the experimentally obtained quadrupole parameters \([14]\).

### 3. Conclusions

Pulsed NMR and NQR methods can be successfully used to study the electronic and magnetic properties of promising thermoelectric compounds with chalcopyrite and delafossite structures. The advantage of the studied multicomponent semiconductor compounds over the currently widely used thermoelectric materials is that they are technologically advanced, resistant to high temperatures, inexpensive, and do not contain toxic substances.

### 4. References

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