

# Application of radio spectroscopy methods for the study of thermoelectrics with a chalcopyrite structure

© V.L. Matukhin<sup>1</sup>, A.N. Gavrilenko<sup>1,¶</sup>, E.V. Shmidt<sup>1</sup>, S.B. Orlinskii<sup>2</sup>, I.G. Sevastianov<sup>1</sup>, S.O. Garkavyi<sup>1</sup>, J. Navratil<sup>3</sup>, P. Novak<sup>3</sup>

<sup>1</sup> Kazan State Power Engineering University,  
420066 Kazan, Russia

<sup>2</sup> Kazan Federal University,  
420008 Kazan, Russia

<sup>3</sup> Institute of Physics of the Czech Academy of Sciences,  
16200 Praha 6, Czech Republic

¶ E-mail: ang\_2000@mail.ru

Received September 19, 2021

Revised September 24, 2021

Accepted September 24, 2021

Doped chalcopyrite compounds are considered. The results of studying the spectral parameters by the <sup>63,65</sup>Cu NMR method in a local field, as well as by the EPR method in the temperature range 15–300 K are presented. The observed broadening of the resonance lines of the NMR spectra and the detection of a paramagnetic signal in the sample at a temperature of 15 K indicate the appearance of anti-structural defects. The rapid change in the shape of the EPR spectrum line, in the temperature range 100–130 K, is associated with the structural-phase transition.

**Keywords:** thermoelectrics, chalcopyrite compounds, antisite defects.

DOI: 10.21883/SC.2022.01.53012.23

## 1. Introduction

High-efficient thermoelectric materials attract large attention due to their potential application in power production, especially for recovery of heat that is a by-product of technological processes. Recently it was proposed to use magnetic semiconductors as efficient thermoelectrics [1]. One of the special features of the magnetic semiconductors is a strong connection between carriers and spins of magnetic ions. This strong interaction can result in large effective carriers mass, that can increase Seebeck coefficient with good conductivity of carriers. One of the representatives of this class of compounds is a well-known semiconductor mineral — chalcopyrite CuFeS<sub>2</sub>.

Recent studies have shown the possible improvement of thermoelectric properties of this compound, especially by means of diluted alloying [2,3]. Detailed understanding of structural characteristics changes and processes, occurring during alloying, is required to produce high-efficient thermoelectric compounds.

In this work we present the study of series of compounds of Cu<sub>1-x</sub>Pd<sub>x</sub>FeS<sub>2</sub> ( $x = 0-0.02$ ) using methods of nuclear magnetic resonance (NMR) of <sup>63,65</sup>Cu in local field and electron paramagnetic resonance (EPR). Thermoelectric and transport properties of samples of Cu<sub>1-x</sub>Pd<sub>x</sub>FeS<sub>2</sub> ( $x = 0-0.1$ ) as hot-pressed tablets were studied earlier [4].

## 2. Experiment

Polycrystalline samples with nominal composition of Cu<sub>1-x</sub>Pd<sub>x</sub>FeS<sub>2</sub> ( $x = 0, 0.01, 0.02$ ) were synthesized from

mix of pure elements, observed from Sigma-Aldrich, including Cu (4N portions), Pd (4N powder), Fe (4N granulated) and S (5 powder). Synthesis of samples is described in study [4].

Spectral parameters of NMR of <sup>63,65</sup>Cu in local field in CuFeS<sub>2</sub> were measured using multipulse NQR/NMR spectrometer Tecmag Redstone. Measurement of NMR line shape was performed using quadrature detection by means of spin echo signals registration with incremental passing of frequency range and signal accumulation.

EPR spectra of three samples of Cu<sub>1-x</sub>Pd<sub>x</sub>FeS<sub>2</sub> ( $x = 0, 0.01, 0.02$ ) were examined at stationary X-ray spectrometer ESP-300 in temperature range of 15–300 K. Samples masses were almost the same and equal to ~ 20 mg.

## 3. Results and discussion

Detailed study of resonance lines shape showed their asymmetric nature with flattening attenuation in high frequency area.

Experimental NMR spectrum of Cu compounds at 77 K can be viewed as superposition of two NMR spectra of Cu: first spectrum, consisting of low-frequency resonance lines, related to the main phase (blue lines  $l_1, l'_1, c_1, c'_1, h_1, h'_1$  in Fig. 1), and the second spectrum, consisting of high-frequency lines, conditioned by resonance centers, located in defected areas of crystal texture (red lines  $l_2, l'_2, c_2, c'_2, h_2, h'_2$  in Fig. 1).

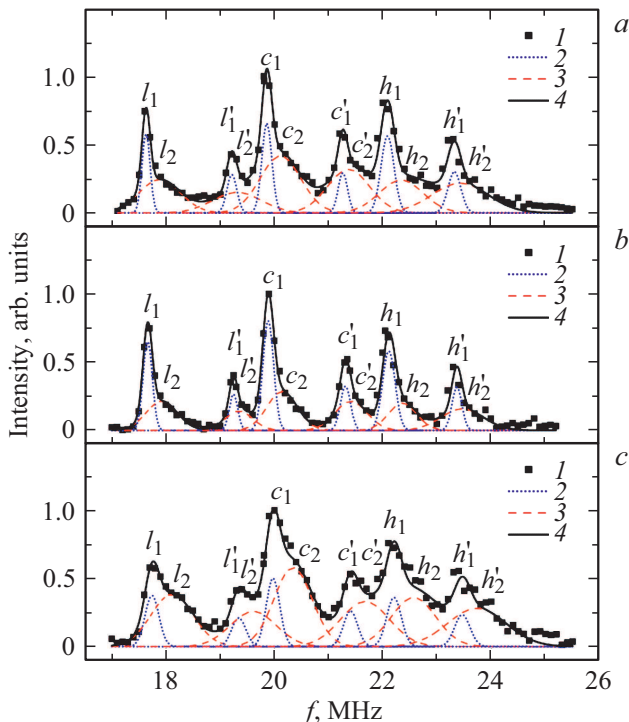
Widening of resonance lines can be result of increase of defects quantity in crystal lattice of the compound,

resulting in higher scatter of electric field gradient (EFG) on resonance copper nuclei. Formation of such defects ( $\text{Fe}_{\text{Cu}}^{2+}$  antisite (AS) defects as proposed in study [4]) is caused by PdS phase formation in chalcopyrite matrix with increase of nominal content of Pd. Frequency shift of resonance lines can be explained with Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction [5]. This is evidenced by increased conductivity of the sample of  $\text{Cu}_{0.98}\text{Pd}_{0.02}\text{FeS}_2$  [4].

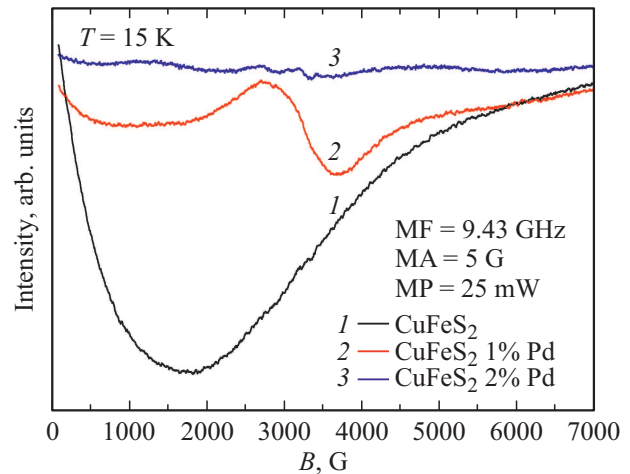
EPR spectra of all samples have their peculiarities. Significant shift of the line center to the right and its narrowing in sample of  $\text{CuFeS}_2$  (0% Pd) are observed in temperature range of 100–130 K.

At low temperature of  $T = 15\text{ K}$  there is almost no wide ferromagnetic signal part in the sample with Pd content of 1%, as opposed to the previous sample without Pd; however, there is presumably a paramagnetic signal with  $g$ -factor, equal to 2.08, and width of  $\sim 1\text{ kHz}$  (Fig. 2), that is gradually weakening and narrowing with temperature increase. In sample with Pd content of 2% the signal near  $g = 2.00$  has the lowest intensity (Fig. 2). It has the same behavior in sample with Pd content of 1% in case of heating.

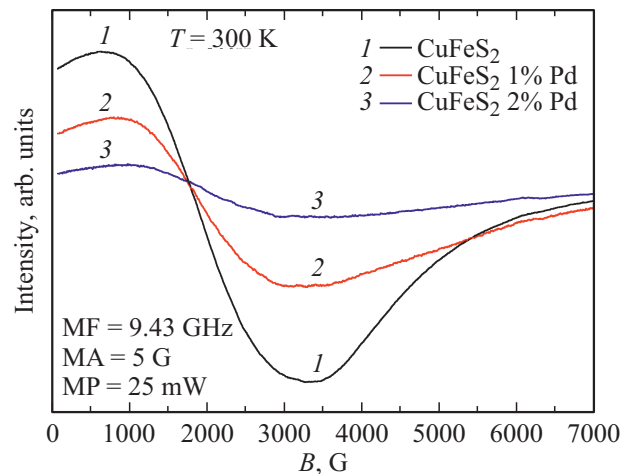
At temperature of 150 K and higher the temperature dependence profile is the same for all samples. Lines shape of all samples is also the same in this temperature range, but



**Figure 1.** NMR spectra of  $^{63,65}\text{Cu}$  in local field at temperature of 77 K of samples of  $\text{CuFeS}_2$  (a),  $\text{Cu}_{0.99}\text{Pd}_{0.01}\text{FeS}_2$  (b) and  $\text{Cu}_{0.98}\text{Pd}_{0.02}\text{FeS}_2$  (c). 1 — experimental data, 2 — narrow line ( $l_1, l'_1, c_1, c'_1, h_1, h'_1$ ), 3 — wide line ( $l_2, l'_2, c_2, c'_2, h_2, h'_2$ ), 4 — accumulation line. The figure shows dotted (2) and dashed (3) curves, indicating splitting of each resonance line of (1 or 4) into two pairs of lines.



**Figure 2.** EPR spectra at temperature of 15 K of samples of  $\text{CuFeS}_2$  (1),  $\text{Cu}_{0.99}\text{Pd}_{0.01}\text{FeS}_2$  (2) and  $\text{Cu}_{0.98}\text{Pd}_{0.02}\text{FeS}_2$  (3).



**Figure 3.** EPR spectra at temperature of 300 K of samples of  $\text{CuFeS}_2$  (1),  $\text{Cu}_{0.99}\text{Pd}_{0.01}\text{FeS}_2$  (2) and  $\text{Cu}_{0.98}\text{Pd}_{0.02}\text{FeS}_2$  (3).

there are differences in intensity. EPR spectra of samples at 300 K are presented in Fig. 3.

#### 4. Conclusion

Widening of NMR resonance lines can be result of increase of defects quantity in crystal lattice of the compound, resulting in higher scatter of EFG on resonance copper nuclei. Such defects can include antisite defects of  $\text{Fe}_{\text{Cu}}^{2+}$  (AS). Formation of such defects is caused by PdS phase formation in chalcopyrite matrix with increase of nominal content of Pd. Thus, it was shown that method of NMR of Cu in local field can be used for evaluation of defectiveness of polycrystalline compounds of  $\text{Cu}_{1-x}\text{Pd}_x\text{FeS}_2$  ( $x = 0-0.02$ ).

Quick change of EPR spectra shape was observed in temperature range of 100–130 K in sample of  $\text{CuFeS}_2$ ,

that presumably corresponds to possible structural phase transition.

Paramagnetic signal with  $g$ -factor, equal to 2.08 and width of  $\sim 1$  kHz is observed in EPR spectra of sample of  $\text{CuFeS}_2:\text{Pd}$  1% at temperature  $T = 15$  K, that can be related to formation of antisite defects.

### Acknowledgments

The authors would like to thank Czech research fund for financial support, project No. 18-12761S.

### Conflict of interest

The authors declare that they have no conflict of interest.

### References

- [1] N. Tsujii. *J. Electron. Mater.*, **42**, 1974 (2013).
- [2] H. Takaki, K. Kobayashi, M. Shimono, N. Kobayashi, K. Hirose, N. Tsujii, T. Mori. *Mater. Today Phys.*, **3**, 85 (2017).
- [3] H. Takaki, K. Kobayashi, M. Shimono, N. Kobayashi, K. Hirose, N. Tsujii, T. Mori. *Appl. Phys. Lett.*, **110**, 072107 (2017).
- [4] J. Navratil, J. Kasparova, T. Plechacek, L. Benes, Z. Olmrova-Zmrhalova, V. Kucek, C. Drasar. *J. Electron. Mater.*, **48**, 1795 (2019).
- [5] T. Koyama, M. Matsumoto, S. Wada, Y. Muro, M. Ishikawa. *J. Phys. Soc. Jpn.*, **70**, 3667 (2001).