

The conduction band of the lanthanide doped chromium disulfides $\text{CuCr}_{0.99}\text{Ln}_{0.01}\text{S}_2$ (Ln=La, Ce, Gd): XANES investigations

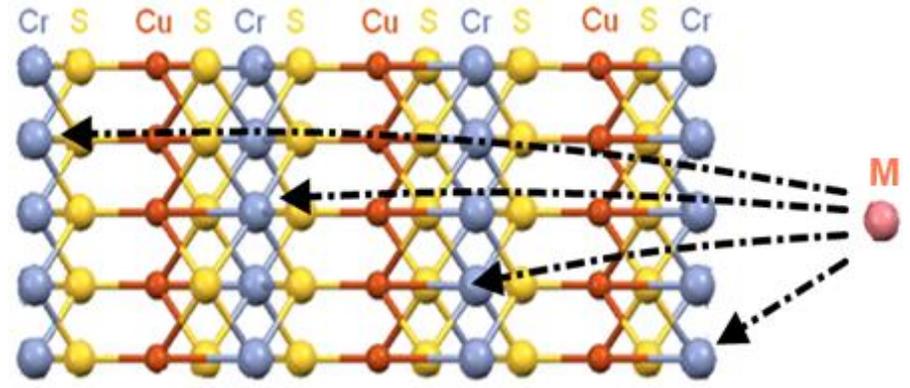
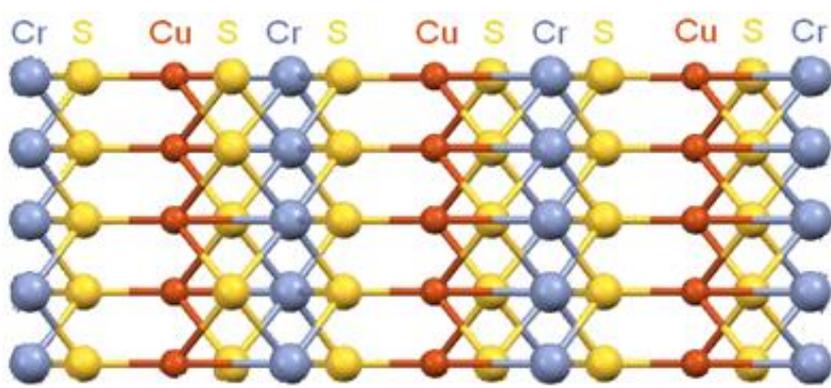
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The layered copper- chromium disulfides



The initial CuCrS_2 - matrix

The solid solutions $\text{CuCr}_{1-x}\text{M}_x\text{S}_2$

The objects of present study are solid solutions based on layered copper-chromium disulfide. The properties of these compound could be modified using cation substitution with the transition metals atoms.

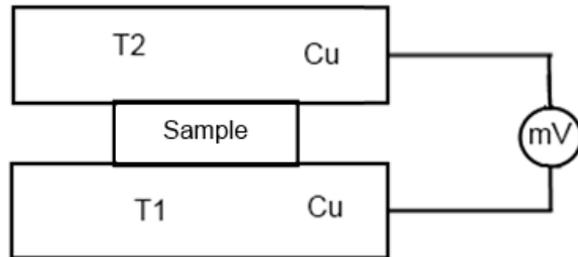
The perspective functional properties of $\text{CuCr}_{1-x}\text{M}_x\text{S}_2$ ($M=\text{V}, \text{Fe}, \text{Mn}, \text{Ti}, \text{Al} \dots$) are :

- ionic conductivity ($10\text{-}100 \text{ (Oh}\cdot\text{cm)}^{-1}$ at $T \sim 670\text{K}$, $M=\text{V}, \text{Fe}, \text{Mn}$ [1]);
- colossal magnetoresistance (200-400 % at $T \sim 100\text{K}$, $H=10 \text{ kOe}$, $M=\text{V}$ [2]);
- metal to insulator transition ($x > 0.15$, $M=\text{V}, \text{Fe}$ [2,3])
- thermoelectric power ($S \sim 400 \mu\text{V/K}$, $M=\text{Fe}$, $x \sim 0\text{-}0.03$ [4,5]).

1. G.R. Akmanova, A.D. Davleshina, Lett.Mater. 3 (2013) 76-78.
2. G.M. Abramova, G.A. Petrakovskii, Low Temp. Phys. 32 (2006) 725-734
3. N. Tsujii, H. Kitazawa, G. Kido, Phys. Stat. Sol. (C). 3 (2006) 4417-4418.
4. A. Kaltzoglou, P. Vaqueiro, T. Barbier, et al , J. Electron. Mater. 43 (2014) 2029-2034
5. E.V. Korotaev, M.M. Syrokvashin, I.Yu. Filatova et al, J. Electron. Mater. 47 (2018) 3392-3397.

Presently the thermoelectric properties of $\text{CuCr}_{1-x}\text{M}_x\text{S}_2$ are in the focus of research.

The thermoelectric materials are capable to produce thermoelectric power under temperature gradient influence.



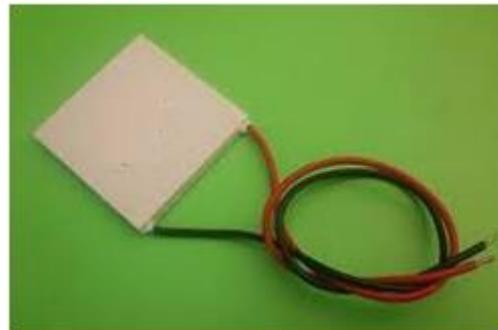
The Seebeck coefficient

$$S = \Delta E / \Delta T$$

Some applications of thermoelectric materials



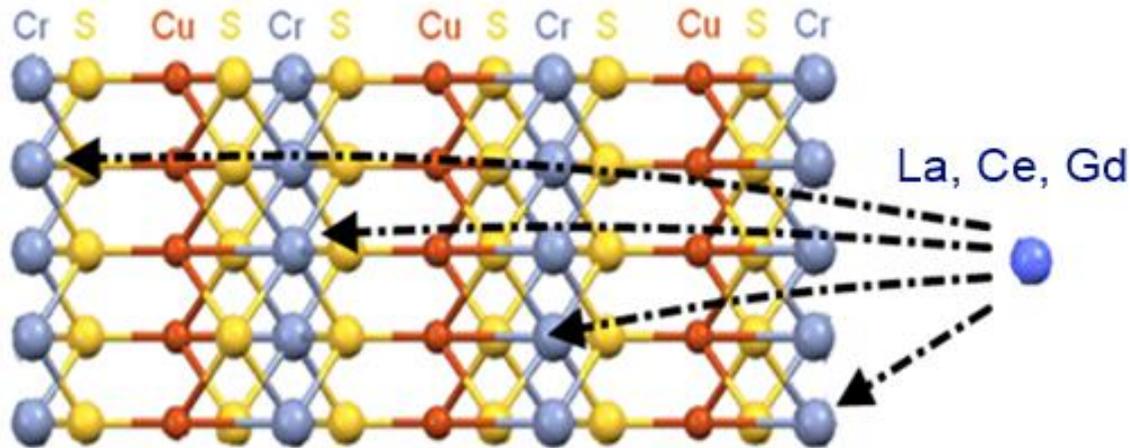
Thermoelectric generator



Peltier element



Thermocouple



The thermoelectric properties of CuCrS_2 -matrix are well investigated, the properties of cation substituted solid solutions are investigated no so detail, especially in the case of lanthanide doped solid solutions.

It was shown [1] that the cationic substitution in the $\text{CuCr}_{1-x}\text{M}_x\text{S}_2$ solutions leads to MIT and thermoelectric properties suppression, but the solution with low dopant concentration could be the perspective materials.

Thus, the investigation of solid solutions $\text{CuCr}_{0.99}\text{Ln}_{0.01}\text{S}_2$ ($\text{Ln}=\text{La, Ce, Gd}$) was carried out.

[1] E.V. Korotaev, M.M. Syrovkashin, I.Yu. Filatova et al, J. Electron. Mater. 47 (2018) 3392-3397

The band theory interpretation of Seebeck coefficient

The Seebeck coefficient of semiconductor materials can be represented as a function of density of states in the valence and conduction bands (the Pisarenko's formula) [1]:

$$S = -\frac{k_B^2}{e} \frac{1}{n\mu_n + p\mu_p} \left\{ \left[2 - \frac{E_F}{kT} \right] n\mu_n - \left[2 - \frac{E_F + E_g}{kT} \right] p\mu_p \right\} = -\frac{k}{e} \left\{ \frac{\left[2 + \ln\left(\frac{N_c}{n}\right) \right] n\mu_n - \left[2 + \ln\left(\frac{N_v}{p}\right) \right] p\mu_p}{n\mu_n + p\mu_p} \right\}$$

N_c , N_v are the effective densities of states for the conduction band and the valence band, n , p , μ_n , μ_p are the concentrations of electrons and holes and their mobility, E_f is the Fermi energy, and E_g is the band gap.

In metals and heavy-doped semiconductors, the Seebeck coefficient depend on the density of states at the Fermi Level according the Mott formula [2]:

$$S = \frac{\pi^2 k_B^2}{3e} \frac{d}{dE} \ln N(E) \Big|_{E=E_f}$$

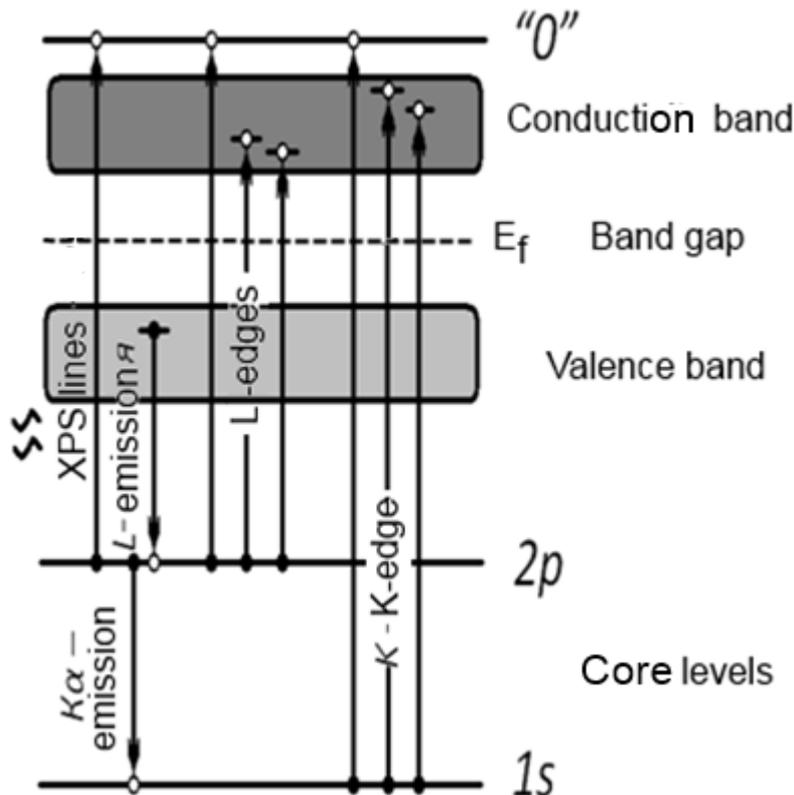
N – density of states at the Fermi level [2].

1.K.V. Shalimova, Semiconductors physics, Moscow: Energoatomizdat, 1985, p. 392.

2. Nikiforov V.N., Morozkin A.V., Irkhin V. Yu., The Physics of Metals and Metallography, 114(2013), 654-666

Thus, the investigation of the thermoelectric materials electronic structure is reasonable

The information on the density of occupied and unoccupied states (DOS) distribution in the valence and the conduction band could be obtained from the quantum chemistry calculations and spectroscopic measurements data.



Using information on the energetic position of pre-edge XANES-spectra transitions, binding energy of initial core levels one could investigate unoccupied states distribution in the conduction band.

XANES spectra shape correction

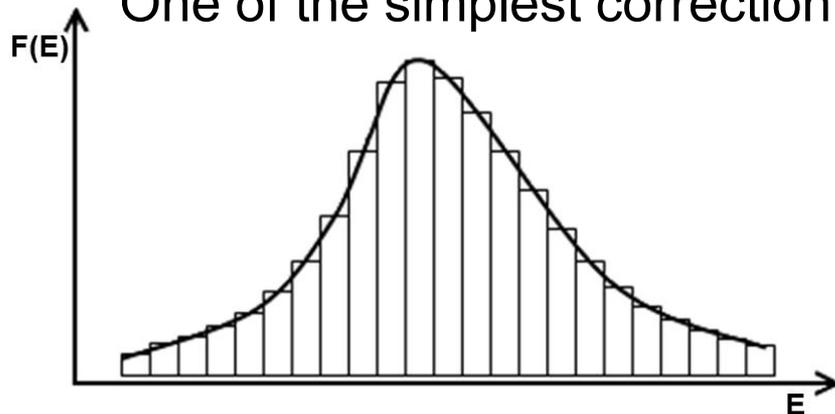
The experimental XANES-spectra shape is broadened due to the experimental spectral resolution and the core level width.

The spectral resolution could be improved, the core level width is fundamental restriction.

The technique for correcting the shape of X-ray spectra is based on solving a convolution type equation:

$$F(E) = \int_{-\infty}^{+\infty} f(E) \varphi(E - E_0) dE \quad (1)$$

One of the simplest correction methods is the “columns method”.



The experimental curve is divided into sections of width $\beta / 2$.

For a single column of a fixed width β the solution is [1]:

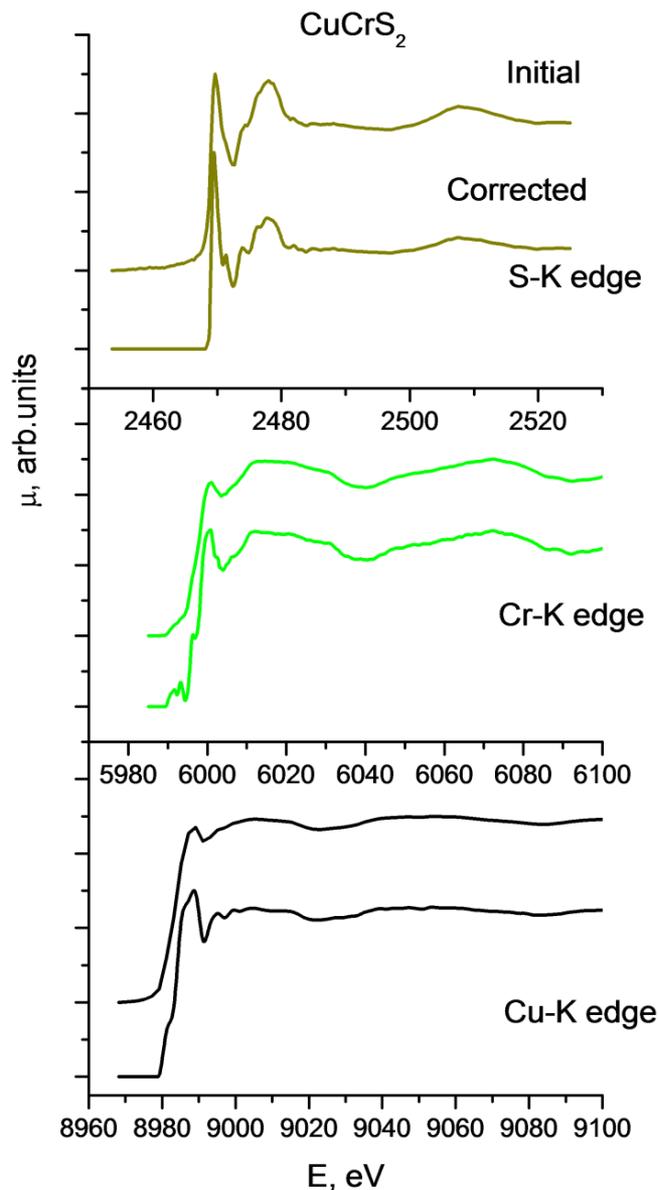
$$f(E) = \frac{1}{\pi} \sum_{m=1}^n (-1)^{m-1} \frac{n!}{m!(n-m)!} \left[\arctg \frac{E + \beta / 4}{m-1} - \arctg \frac{E - \beta / 4}{m-1} \right] \quad 10 \leq n \leq 15 \quad (2)$$

XANES spectra registration

X-ray absorption edges of copper and gadolinium atoms in the samples under study were obtained by a standard transmission mode using synchrotron radiation at VEPP-3 storage ring on the station "EXAFS spectroscopy" in Siberian Synchrotron and Terahertz Radiation Centre (Budker Institute of Nuclear Physics SB RAS, Novosibirsk).

X-ray absorption edges of chromium and sulfur atoms were obtained by a standard transmission mode using synchrotron radiation at VEPP-4 storage ring on the metrology station "Cosmos" in SSTRC.

XANES spectra shape correction demonstration

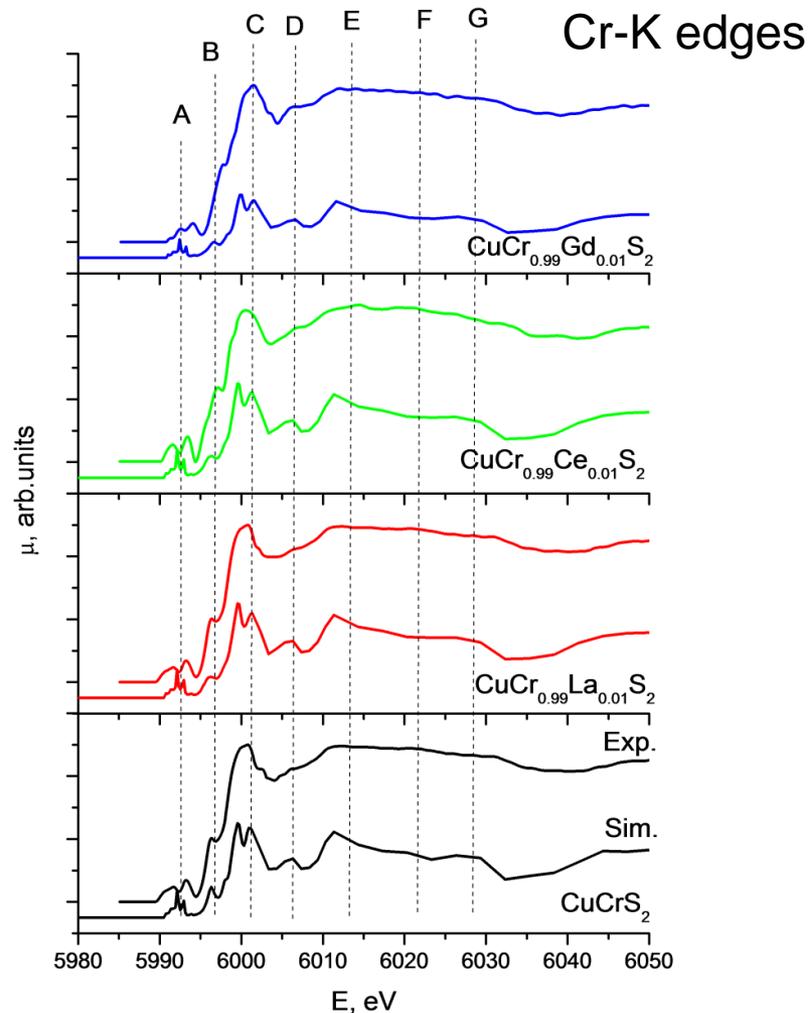
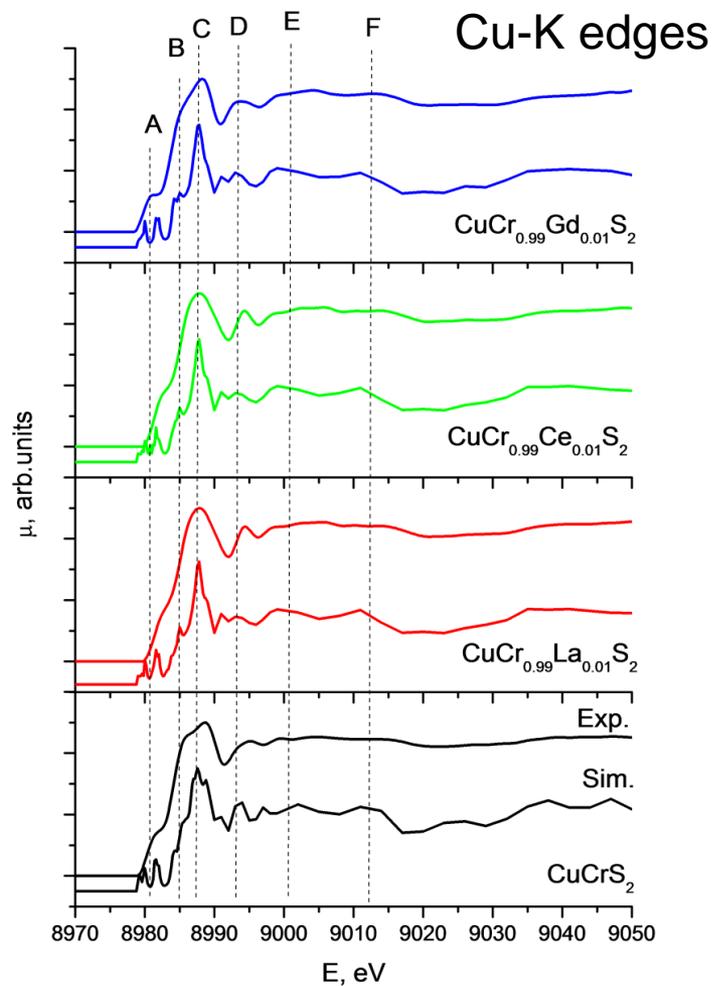


The distortion function width was taken as superposition of core level width and spectral broadening.

After spectra shape correction the fine XANES structure features become sharper.

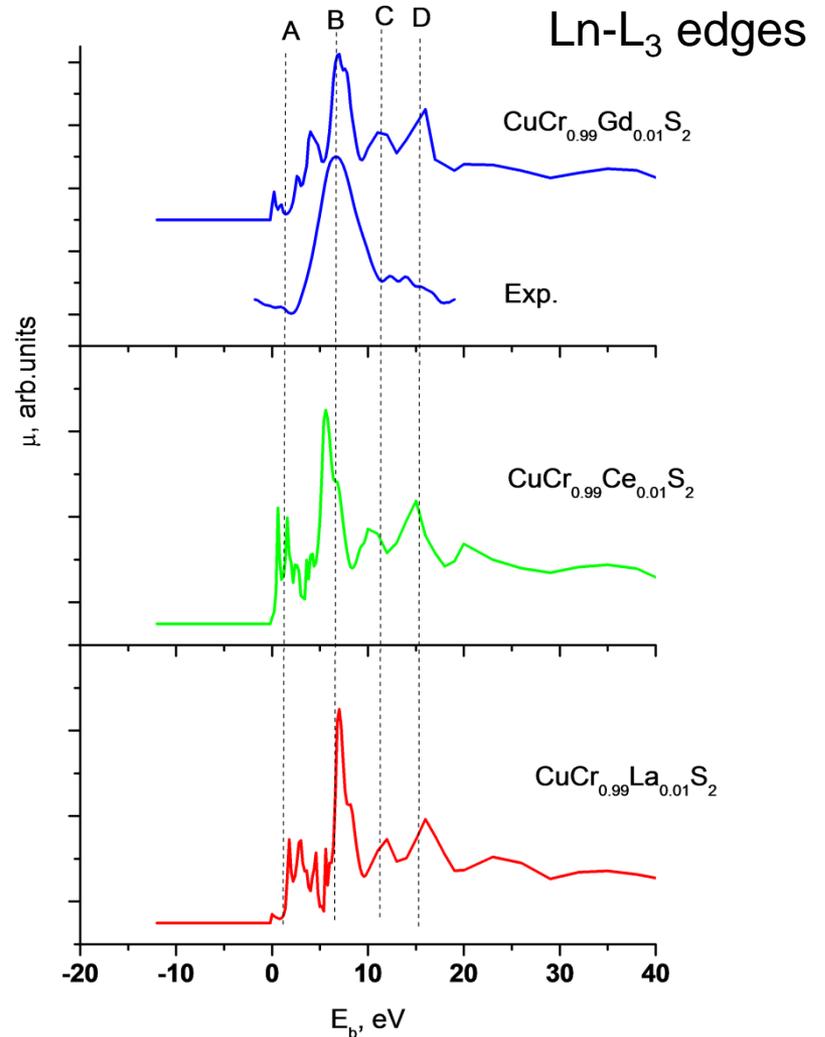
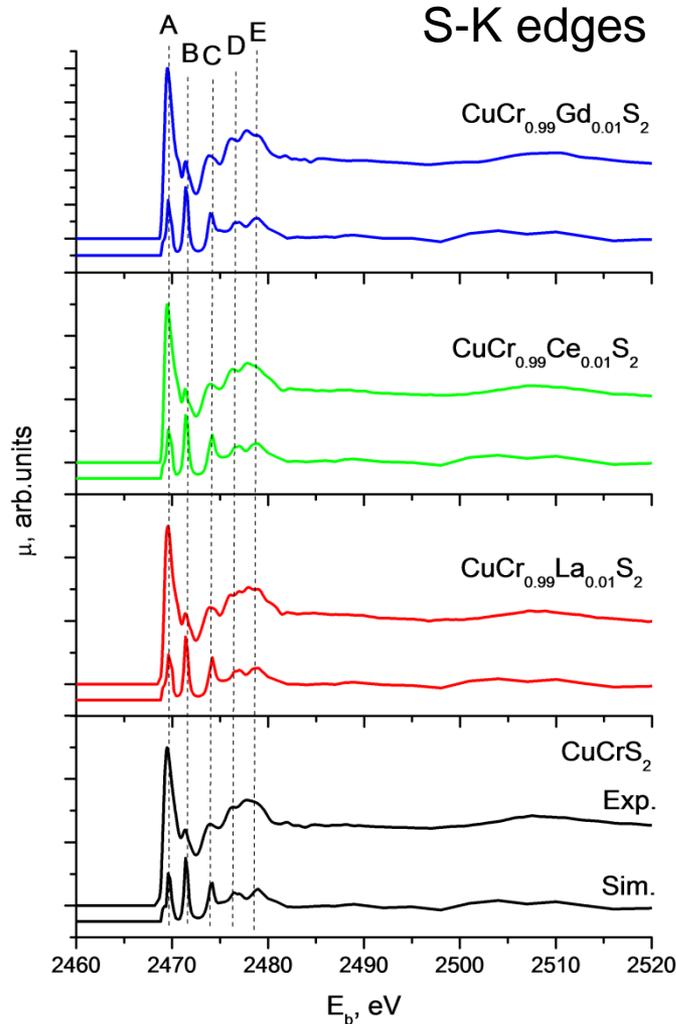
In order to interpret the X-ray absorption edges fine structures the theoretical simulation of XANES spectra was carried out using the finite difference method (FDMNES software package).

XANES spectra simulation



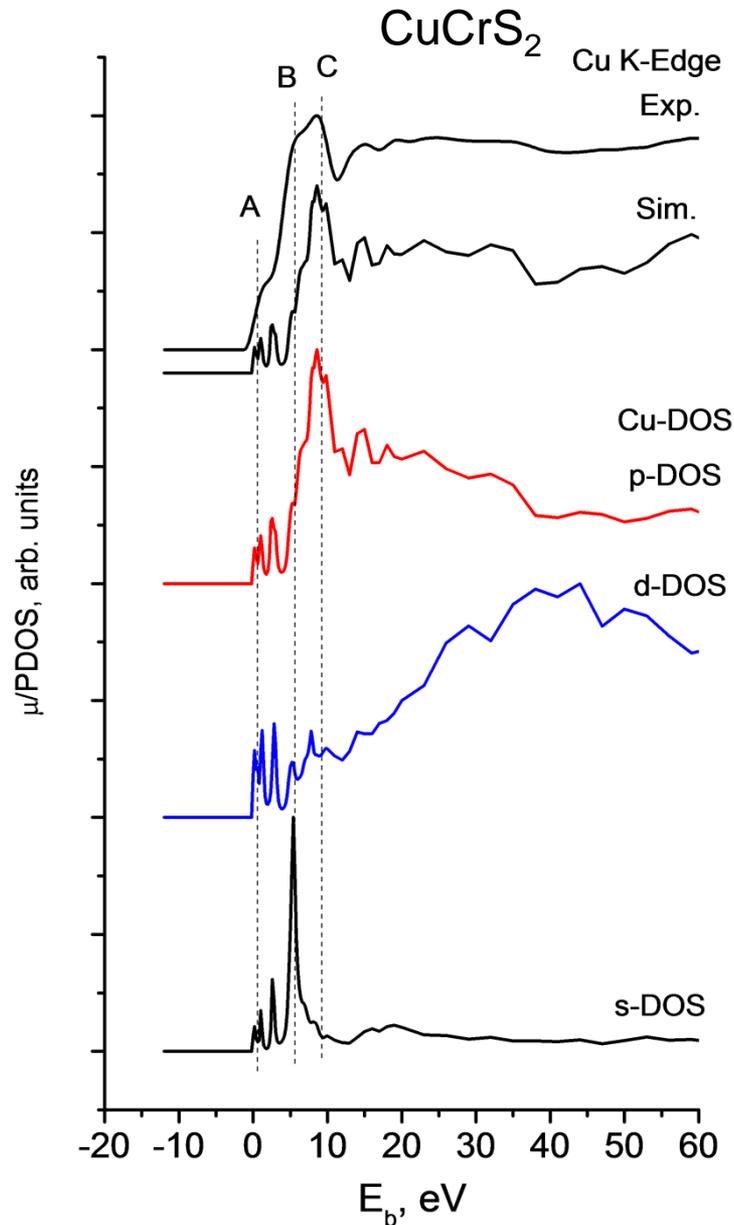
The experimental XANES spectra shape and results of finite difference method simulation are in good agreement. The Cu, Cr, S K-edges fine structure character preserved after cationic substitution.

XANES spectra simulation



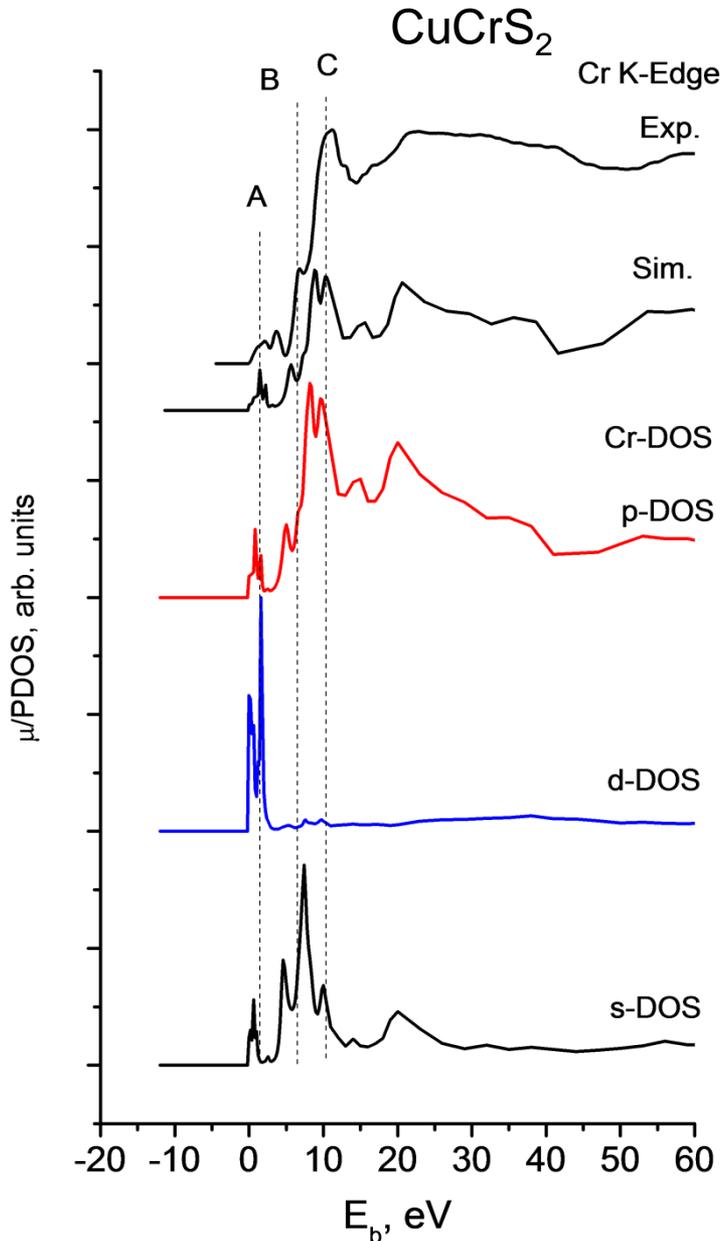
That fact indicate that the local atomic environment in the lanthanide-doped solid solutions $\text{CuCr}_{0.99}\text{Ln}_{0.01}\text{S}_2$ remains unaffected after cationic substitution. The theoretical simulations predict the similarity of the Ln L₃ edge structures. The Ln L₃ spectral shape evolution under the Ln type change could be due to the unoccupied f-DOS changing.

Density of states and Cu K-edges interpretation



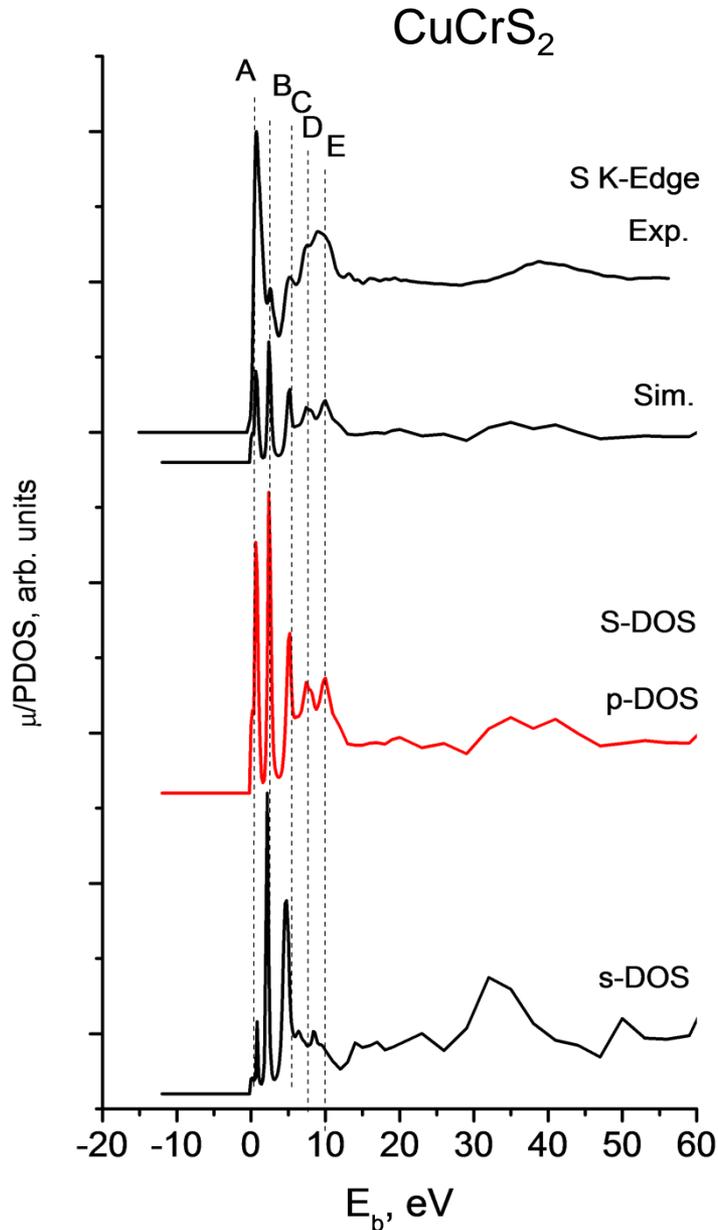
The Cu K-edge was presented in the binding energy scale using data on the Cu $K\alpha_1$ transition ($1s \rightarrow 2p_{3/2}$) and the XPS Cu $2p_{3/2}$ binding energy. The comparison of the Cu K edge fine structure and theoretical DOS simulation exhibit that the unoccupied p-DOS determinate the edge structure. From the other side there is correlation between the p-, d- and s-DOS maxima near the conductivity band bottom (feature A area). The s-DOS absolute maximum is situated in the area of feature B. Since the $1s \rightarrow s$ transition is forbidden that correlation could be due to the s-p states hybridization. The d-DOS maxima are situated in high energy area.

Density of states and Cr K-edges interpretation



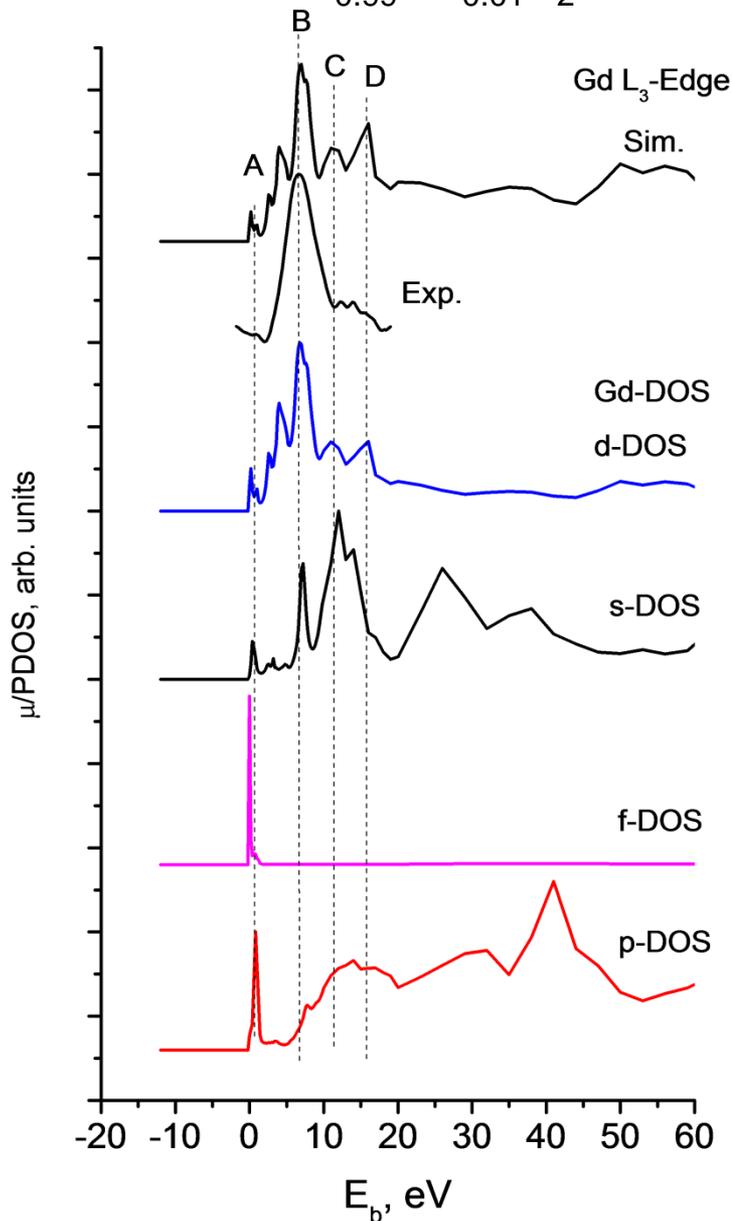
The comparison of the Cr K edge fine structure and theoretical DOS simulation exhibit that the unoccupied p-DOS determinate the edge structure. The correlation between the p-, d- and s-DOS maxima near the conductivity band bottom (feature A area) could be seen. The s-DOS absolute maximum is situated in the area of feature B. The d-DOS maxima are situated near the conductivity band bottom. Taking into account the high density of Cr unoccupied d-states the quadrupole $1s \rightarrow d$ transition contribution could be essential for feature A structure.

Density of states and S K-edges interpretation



The comparison of the S K-edge fine structure and theoretical DOS simulation exhibit that the unoccupied p-DOS determinate the edge structure. The correlation between the p-DOS and s-DOS maxima in the large energetic area could be seen.

Density of states and Gd L₃-edge interpretation

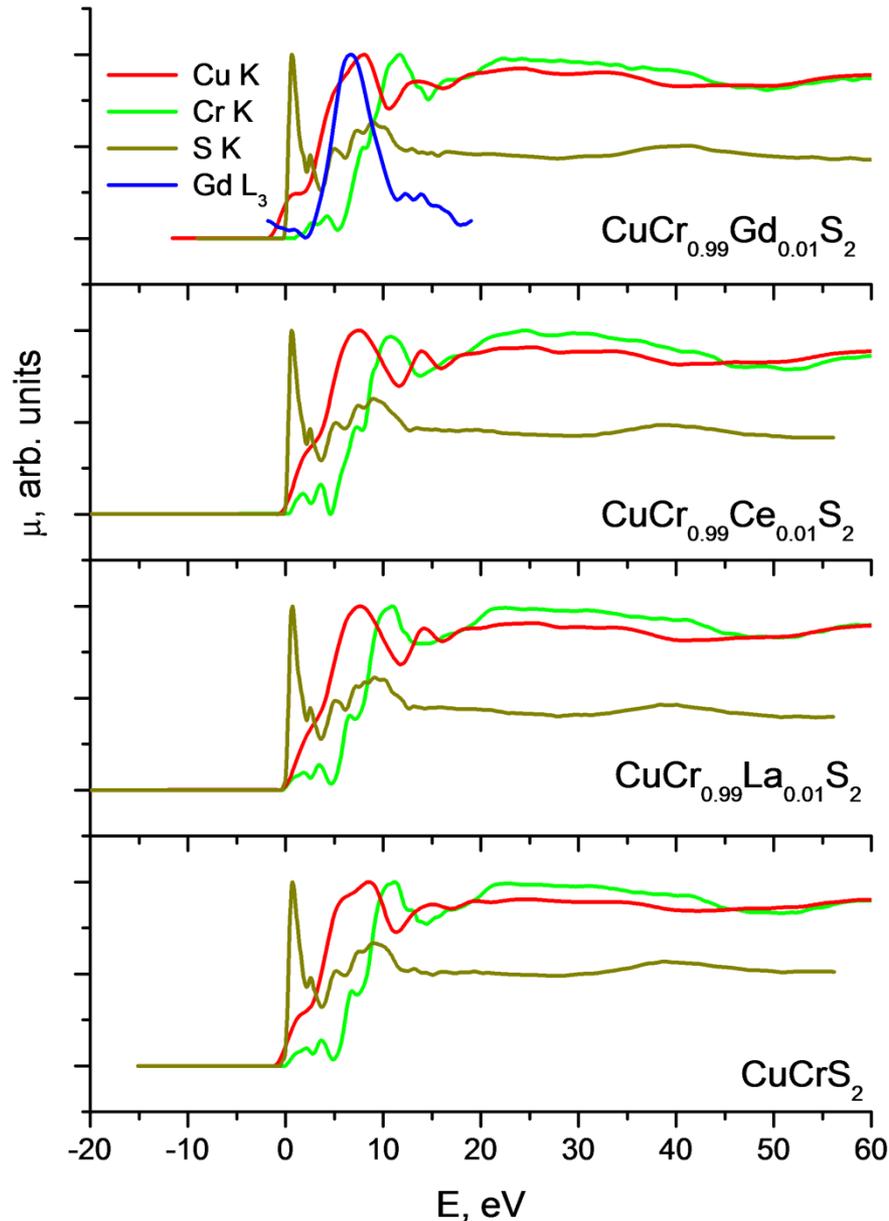


The Gd L₃-edge was presented in the binding energy scale using theoretical ionization potential (FDMNES).

The Gd L₃-edge spectral shape is most complicated due to the p→d and p→s dipole transitions probability. Thus, the edge spectra is determined by the superposition of d-DOS and s-DOS.

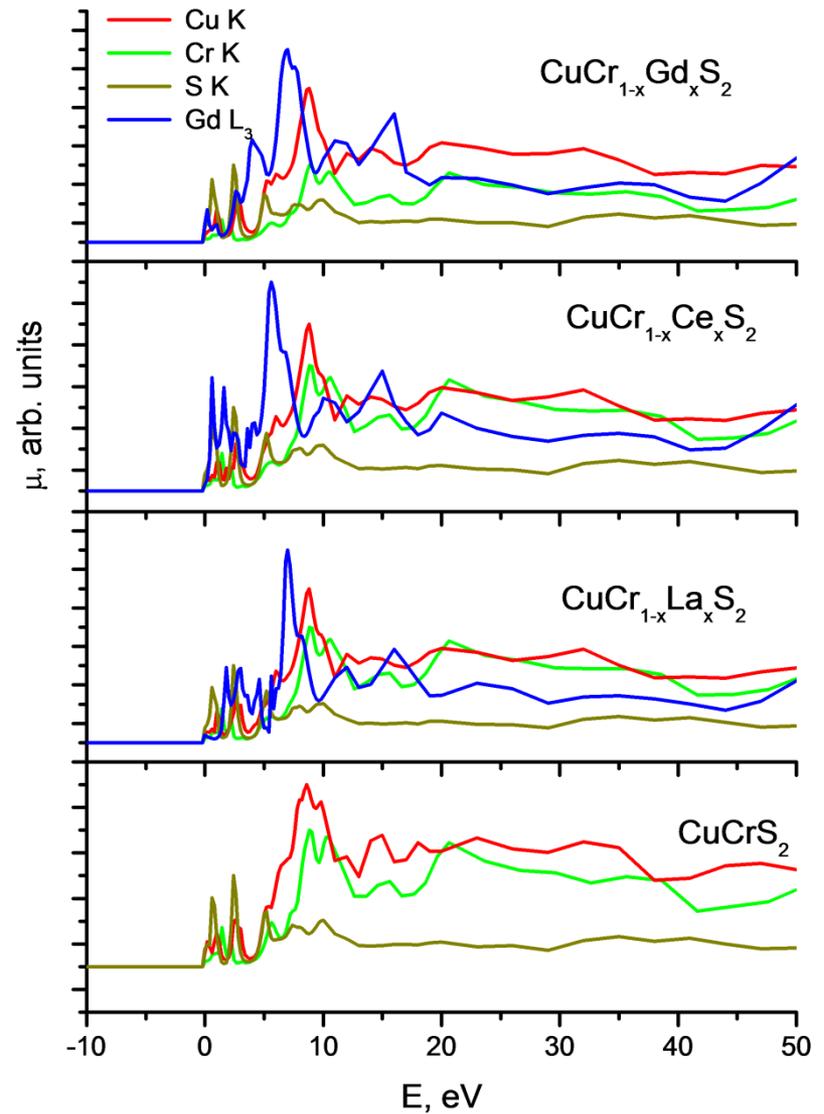
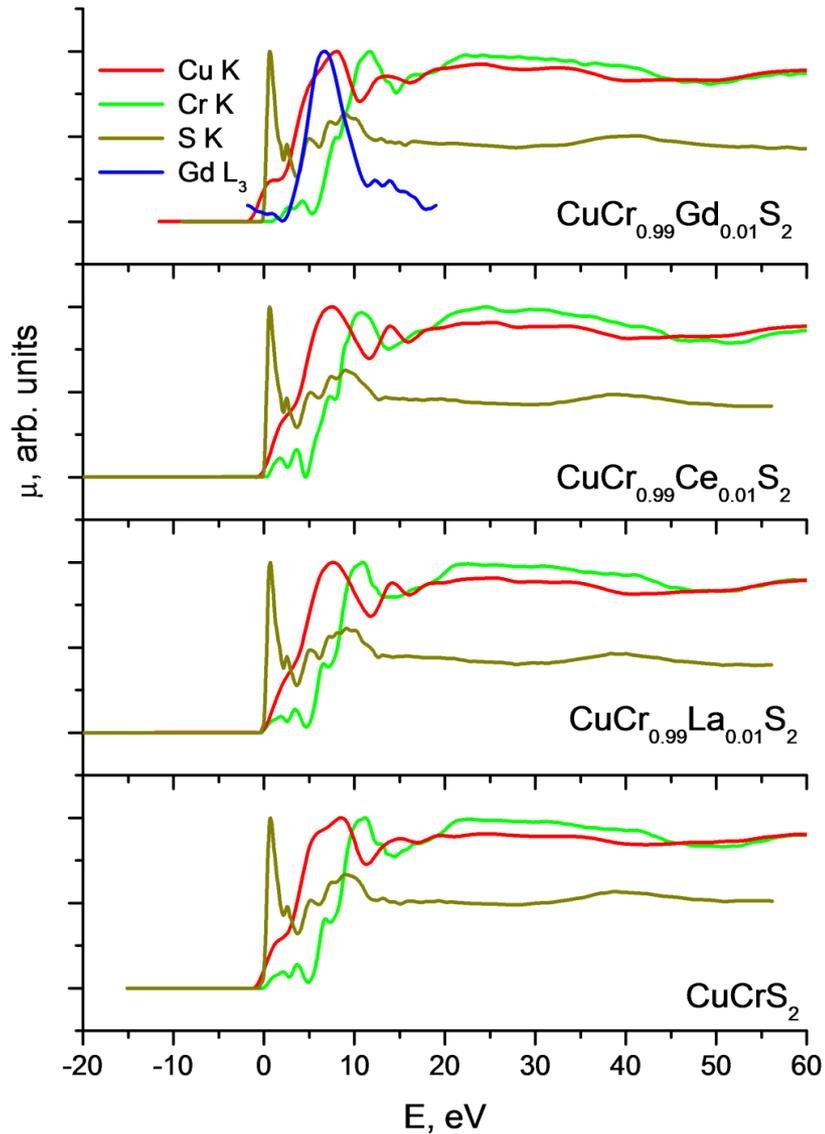
The correlation between the s-, p-, d- and f-DOS maxima near the conductivity band bottom could be seen (feature A area). The f-DOS maxima is situated near the conductivity band bottom. Taking into account the high density of Gd unoccupied f-states the quadrupole p→f transition contribution could be essential for feature A structure.

Conduction band XANES investigation



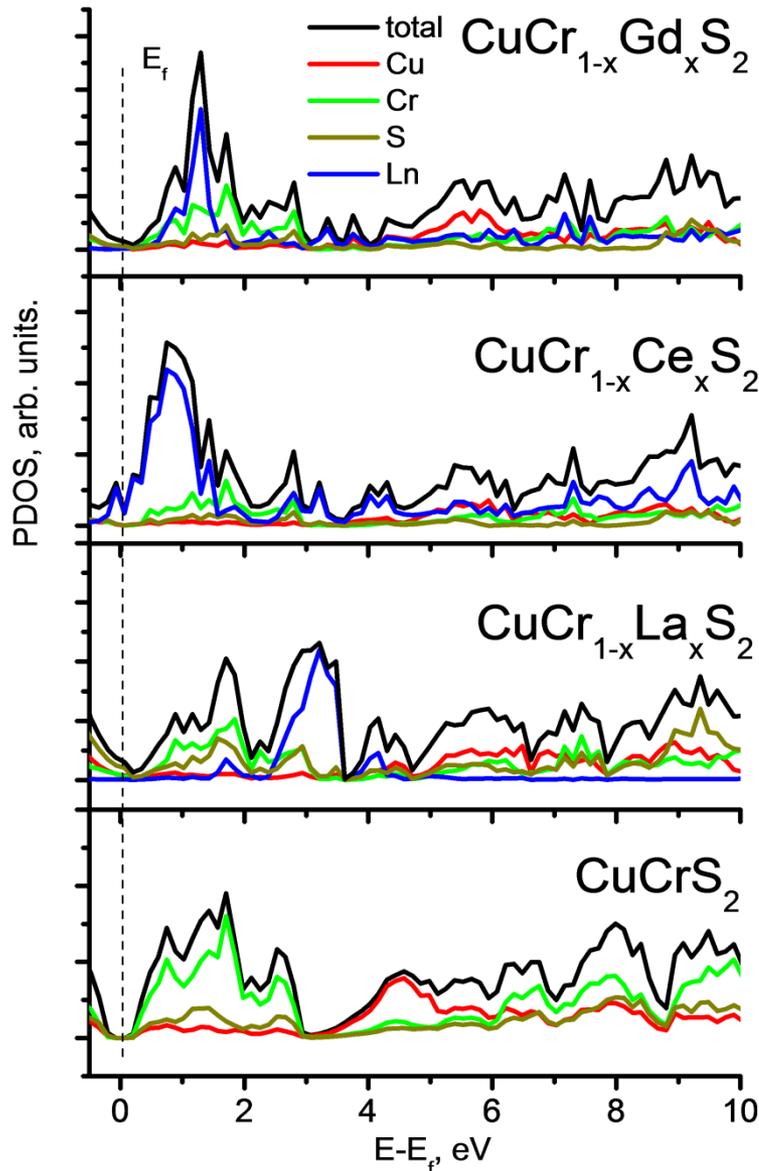
Taking into account previously interpreted XANES-spectra one could suggest that the conduction band bottom of CuCrS_2 is formed mainly with the contribution of the mixed Cu s-,p- and d-states, Cr d-states and S p-states. After the cation substitution the f-unoccupied states localize near the conduction band bottom area replacing the chromium d-states. The unoccupied Cu, Cr, S states distribution character is preserved after cation substitution.

Conduction band XANES investigation



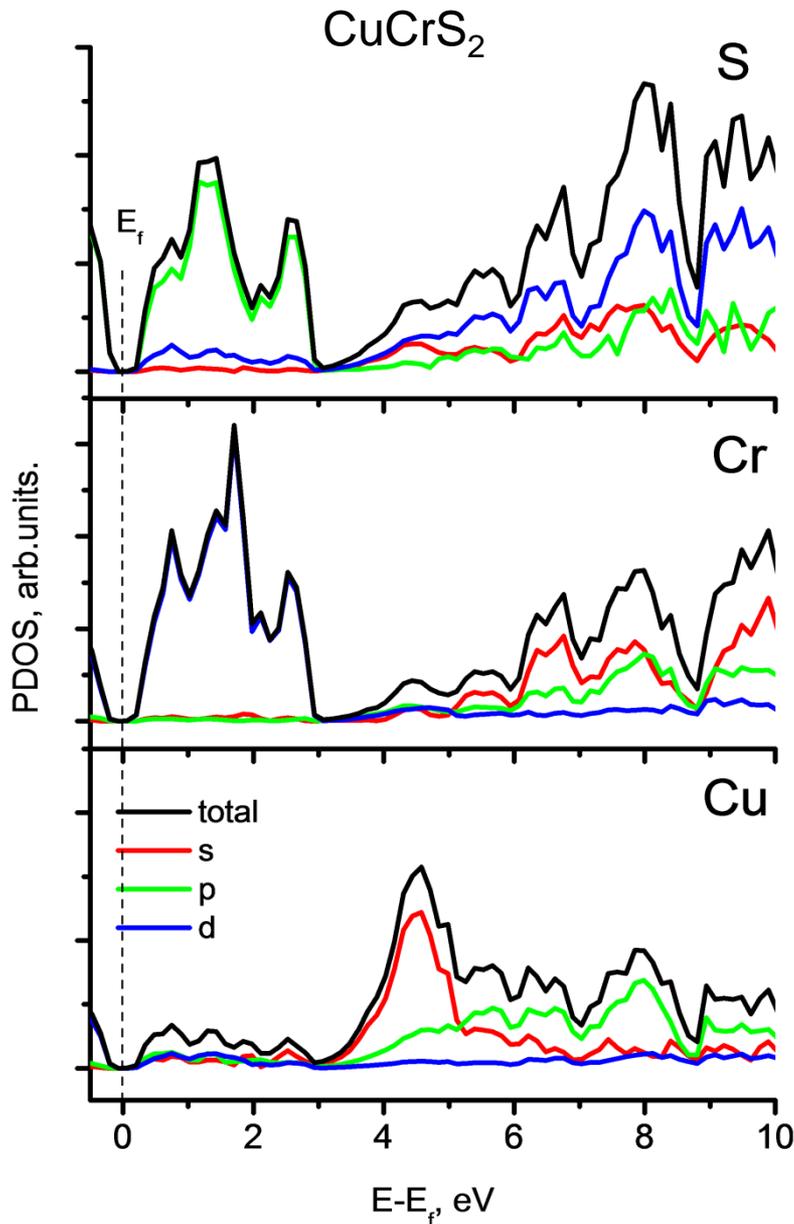
The experimental data and the simulation results agree well.

Conduction band simulations



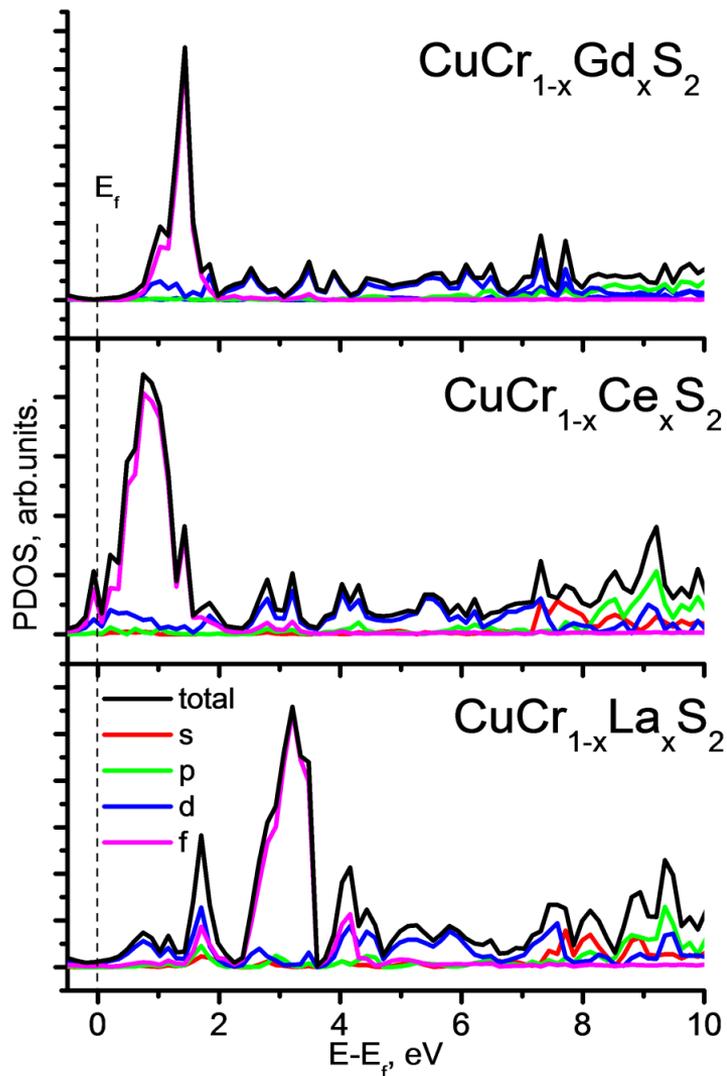
In order to detail investigate DOS – distribution near the conduction band bottom the DFT simulation was carried out using the BAND software package (TZP basis set, GGA approximation, PBE Sol exchange correlation potential). In the case of initial CuCrS_2 -matrix the conduction band bottom structure is determined by the Cr states contribution. The unoccupied Cu, Cr, S states distribution character is preserved after cation substitution. For the Ln-substituted solid solutions the conduction band bottom is affected with the Ln contribution that prevail replacing the chromium states. Cationic substitution of Cr atoms with lanthanide atoms leads to the metal to insulator transition (model $x \approx 0.33$).

Conduction band simulations

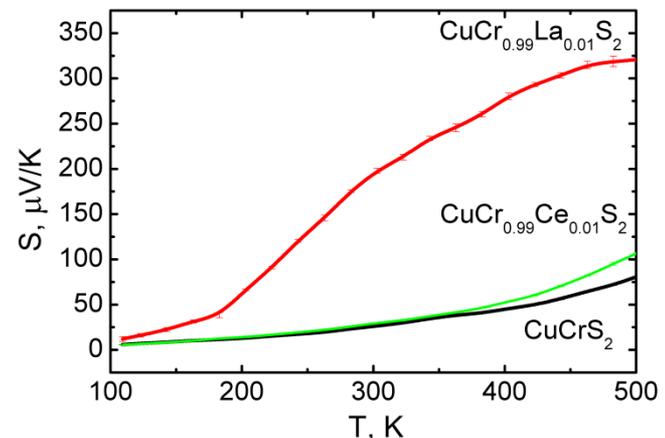


In the case of initial CuCrS₂ the copper DOS distribution near the conduction band bottom is presented by the mixing of s-,p- and d-states. The contribution of chromium states near the conduction band bottom is determined by the d-states. The sulfur DOS near the conduction band bottom is determined by p-states contribution.

Conduction band simulations



The La unoccupied states contributions in investigated solid solutions are determined by f-states. The Ce and Gd contributions near the conduction band bottom are determined by the f-states. In the case of La-doped solid solutions the La contribution in conduction band bottom is determined by the d-states. The La f-states main contribution is shifted into the high energy area. That fact allows one to predict that the properties of La-doped solid solutions differ significantly from other Ln-doped solid solutions.



For example, $\text{CuCr}_{0.99}\text{La}_{0.01}\text{S}_2$ demonstrates ~ 4 times increase in S value compared to CuCrS_2 [1]. Thus, the conduction band simulations not contradict with the XANES investigations and simulations results.

Conclusion

The comprehensive theoretical and experimental investigation of the doped solid solutions $\text{CuCr}_{0.99}\text{Ln}_{0.01}\text{S}_2$ (Ln=La, Ce, Gd) conduction band was carried out. It was shown:

1. The Cu, Cr, S K-edges fine structure character preserved after cationic substitution. That fact indicates that the local atomic environment in the lanthanide-doped solid solutions $\text{CuCr}_{0.99}\text{Ln}_{0.01}\text{S}_2$ remains unaffected after cationic substitution.
2. The Ln L_3 spectral shape evolution under the Ln type change could be due to the unoccupied f-DOS change.
3. The conduction band bottom of CuCrS_2 is formed mainly with the contribution of the mixed Cu s-,p- and d-states, Cr d-states and S p-states.
4. After the cation substitution the unoccupied f- states localize near the conduction band bottom area replacing the chromium d-states. The unoccupied Cu, Cr, S states distribution character is preserved after cation substitution.
5. In the case of La doped solid solutions the La f-states main contribution is shifted into the high energy area from the conduction band bottom.

Acknowledgements

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The X-ray absorption spectra were measured using the shared research center SSTRC on the basis of the Novosibirsk VEPP-4 - VEPP-2000 complex at BINP SB RAS, using equipment supported by project RFMEFI62119X0022.

Thank you for attention!