

Bond length determination in Cu-Mg-O by EXAFS spectroscopy

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Magnetic semiconductors such as $\text{Cu}_x\text{Mg}_{1-x}\text{O}$, which are perspective materials for high-temperature superconductivity have been studied by EXAFS. The new technique of obtaining information from EXAFS-data has been described. It is based on the special iterative algorithm of solving an inverse ill-posed problem on the determination the partial pair correlation functions (pPCFs). Bond lengths of the nearest neighbours have been determined. It was clearly shown that the short range order in compound $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ differs from a hypothetical alloy with MgO structure and from the copper oxide.

Keywords: high-temperature superconductivity, regularization method, partial pair correlation function

1. Superconductivity and copper oxide

The structural study of new materials with unique characteristics allows to understand the origin of their properties. Also the search for new consistent compounds is very popular. Some such of interesting materials are the high-temperature superconductors. The investigations carried out in the Institute of Metal Physics, Ekaterinburg (Samokhvalov *et al.*, 1998) on basis of copper oxide have shown, that there exist the localized areas of superconductive phase in partially restored samples of CuO. The volume of the phase was found 2-3%, and the critical temperature up to 200-300K. This kind of material has been called the compound with a localized ("impurity") superconductivity. The presence of "diamagnetic" anomalies in temperature dependence of magnetizability, electron spin resonance and effects of magnetic shielding give evidence of superconductivity.

Among the probable reasons of high-temperature localized superconductivity might be the formation the CuO impurity with NaCl structure. But the bulk sample CuO with NaCl structure has not yet synthesized up to now. X-ray study of the similar compound – $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ (Samokhvalov *et al.*, 1999) shows that there is a single phase with NaCl structure. The present work is devoted to the short range order investigation of this solid state solution.

2. Samples and model

The sample $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ has been prepared by annealing the pressed mixture of pure powders CuO and MgO taken in the appropriate proportion (1:4), on air at temperature 1050°C during 50 hours. CuO has the monoclinic lattice with 4 copper atoms and 4 oxygen atoms in an elementary cell with parameters $a=4.6837\text{Å}$, $b=3.4266\text{Å}$, $c=5.1288\text{Å}$, $\beta=99.54^\circ$. The MgO structure also is known – it is the NaCl type structure with lattice parameter $a=4.208\text{Å}$. The results of X-ray scattering study of the given solid state solution sample have shown that a single MgO-structure phase has lattice parameter $a=4.219\text{Å}$.

On the basis of X-ray scattering investigation the hypothetical MgO-based structure model has been constructed. In a MgO lattice with parameter $a=4.219\text{Å}$ the Cu atoms randomly replace Mg atoms according to the concentration (20%). The assumption has been made that in $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ Cu atoms locate in NaCl-type lattice as Mg atoms in MgO do. On the basis of atoms distribution in real space the model partial pair correlation functions $g_{\text{Cu-Cu}}(r)$, $g_{\text{Cu-Mg}}(r)$, $g_{\text{Cu-O}}(r)$, and then the model normalized oscillating part of absorption spectra near Cu K-edge in reciprocal space have been constructed to be compared with our experimental results.

The CuO sample of with well-known structure has been studied to evaluate a new method of pPCF determination. Also CuO has been used as a reference sample to obtain the dispersion law between energy and reciprocal space. So, in contrast to the conventional procedure there is no need to use E_0 as a fitting parameter.

3. Experiment

X-ray absorption spectra have been collected on laboratory spectrometer RAS-1 (Institute of Metal Physics, Ekaterinburg) near Cu K-edge. SiO_2 (1340) monochromator has been used, collected statistic was about 10^6 , resolution about 1.2eV. The samples with the thickness 15 μm for CuO and the thickness 56 μm for $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ have been prepared from powder materials. As a result of the small sample thickness the absorption spectrum of copper oxide turned out distorted by thickness inhomogeneity effect. The procedure of correction (Ryazhkin *et al.*, 2000) has been applied. As a result amplitude has been grown on 30%. In all other respects, the usual preliminary processing has been used (Babanov *et al.*, 1997). Experimental normalised oscillating part of the absorption spectra of $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ is shown in Fig.1. A model EXAFS-spectrum for a hypothetical alloy $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ with MgO structure and experimental CuO data also are depicted.

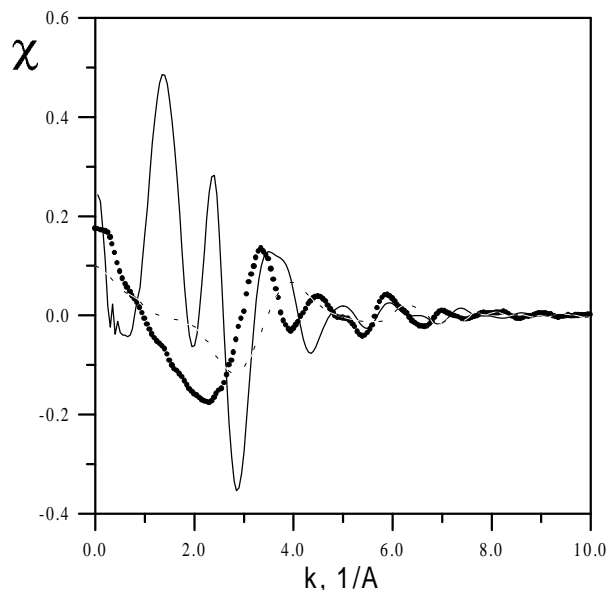


Figure 1
EXAFS-spectra for $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ (points), MgO-based model for $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ (solid line) and CuO (dashed line)

4. Mathematical procedure

For the determination of local atomic structure the method different from conventional methods (fitting method, Fourier-transformation) has been used. It is based on the solution of the inverse problem without any model assumptions and has some advantages (Babanov *et al.*, 1981, Ershov *et al.*, 1981). As a result, partial pair correlation functions (pPCFs) could be obtained "as it is". From this function one can determine structure parameters: interatomic distances, coordination numbers, D-W factors. In the case of usual FEFF/fit methods for three component compound no less than nine parameters strongly correlated with each other have to be fitted. From Cu-edge EXAFS data for a copper oxide two pPCFs $g_{Cu-Cu}(r)$, $g_{Cu-O}(r)$ could be found, but for a solid state solution $Cu_{0.2}Mg_{0.8}O$ it here three of them – $g_{Cu-Cu}(r)$, $g_{Cu-Mg}(r)$ and $g_{Cu-O}(r)$. From the formal algebraic logic at least three experimental data sets are required to find three unknown functions with all true parameters. It is necessary to note that in this work the determination of three pPCFs from one EXAFS data set for compound with the unknown structure has been made for the first time. The connection between the normalised oscillating part of the absorption spectra of the n -component compound and $g_{ij}(r)$ in a single scattering approach can be described as:

$$\chi_i(k)k = 4\pi\rho_0 \times \sum_{j=1}^n c_j \int_0^{\infty} f_j(k,r)g_{ij}(r)e^{\frac{-2r}{\lambda_i(k)}} \times \sin(2kr + 2\delta_i(k) + \varphi_j(k,r) - \pi)dr, \quad (1)$$

where i is a type of the central atom, j is a type of neighbouring atom ($j = 1, 2$ for a binary component compound and $j = 1, 2, 3$ for the three component one), c_j is a concentration of neighbouring atom, $f_j(k,r)$ and $\varphi_j(k,r)$ are backscattering amplitude and backscattering phase, $\delta_i(k)$ is a central phase shift, $\lambda_i(k)$ is a mean free path. Phases, amplitudes and mean free paths have been calculated by the FEFF8 program (Ankudinov *et al.*, 1998). An algorithm of the solution of Fredholm integral equation including a transition to the restricted limits in the reciprocal space, a discretization, a regularization by Tichonov's method has been described in details earlier (Babanov *et al.*, 1981) The first solution is:

$$g_0 = (A^*A + B)^{-1}(A^*U), \quad (2)$$

where A is the matrix describing the integral operator in (1), U is the vector connected with initial experimental data set, g is the vector of target pPCFs, B is the regularization matrix. The next step is an iteration procedure

$$g_m = (A^*A + B)^{-1}(A^*U + Bg_{m-1}), \quad (3)$$

where m is a number of iteration. The previous solution ("simple iteration") or some trial function can be used as the $g_{m-1}(r)$. As a trial function the Gauss function has been used for describing the peaks of the previous solution at the each iteration. Thus, *a priori* physical information has been introduced in algorithm to obtain a reliable solution in condition of insufficient amount of experimental data (one data set for determining three pPCFs).

This procedure, as it has been shown from numerical simulations, may be applied successfully to the compounds with the separate peaks in the partial pair correlation function, which describe the separate shells. The following results of interatomic distances for CuO have been obtained from experimental data: $r_{Cu-Cu} = 2.92 \pm 0.02 \text{ \AA}$ (by the conventional X-ray scattering data – 2.91 \AA) and $r_{Cu-O} = 1.97 \pm 0.01 \text{ \AA}$ (by the conventional X-ray scattering data – 1.96 \AA).

The calculation for the solid state solution $Cu_{0.2}Mg_{0.8}O$ shows that the contribution of the pair Cu-Cu in the normalised oscillating part of the absorption spectrum is very small and has been caused by small Cu concentration and small values of their backscattering amplitudes. The functions $g_{Cu-Mg}(r)$ and $g_{Cu-O}(r)$ have the greater weight and distort $g_{Cu-Cu}(r)$. Then the following procedure has been used:

1. Two "strong" pPCFs $g_{Cu-Mg}(r)$ and $g_{Cu-O}(r)$ are determined from the experimental spectra for $Cu_{0.2}Mg_{0.8}O$.
2. A contribution to EXAFS spectra of $g_{Cu-Mg}(r)$ and $g_{Cu-O}(r)$ is calculated by equation (1). Then this contribution is removed from initial experimental data.
3. This new function contains an information about one function ($g_{Cu-Cu}(r)$) only and processing is practically reduced to the solution of the one-component inverse problem.

This technique has been tested successfully during numerical simulation. In the simulation the model normalized oscillating part of absorption spectra described earlier has been used in consequence of proposed steps (from 1 to 3). Parameters for solving inverse problem have been the same as in the experimental treatment. The errors in distances (coordinates of the first peak in the pPCFs) have been up to 1.5%, the errors in coordination number have been more than 0.5 at. The conclusion has been made that in the case of one experimental data set for determining three unknown functions only some information can be guaranteed.

5. Results and conclusions

Three partial pair correlation functions have been determined for solid state solution $Cu_{0.2}Mg_{0.8}O$ from experimental spectrum. Three-step procedure has been used. Initial $\chi(k)$ spectrum, contribution of $g_{Cu-Mg}(r)$ and $g_{Cu-O}(r)$ (after 1-st step) and residual contribution of $g_{Cu-Cu}(r)$ are drawn in Fig.2.

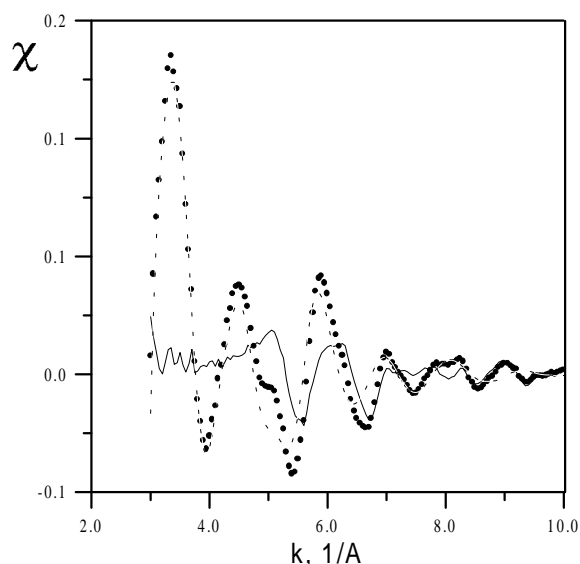


Figure 2 $Cu_{0.2}Mg_{0.8}O$ EXAFS-spectra for 3-step procedure: initial data (points), contribution of $g_{Cu-Mg}(r)$ and $g_{Cu-O}(r)$ (dashed line), residual contribution of $g_{Cu-Cu}(r)$ (solid line). All spectra are drawn with the weights that are proportional to the concentration and amplitude in particular.

As it is marked earlier the $g_{Cu-Cu}(r)$ contribution is sufficiently smaller than others contributions. It seems that the concentration of $c_{Cu} = 0.2$ in this system is the minimum value for reliable determination of $g_{Cu-Cu}(r)$.

The following parameters have been used: interval in the reciprocal space $3.0 - 15. \text{\AA}^{-1}$, step 0.05\AA^{-1} ; intervals in the real space $2.2-10. \text{\AA}$, $1.7-10. \text{\AA}$ and $2.8-10. \text{\AA}$ for $g_{\text{Cu-Cu}}(r)$, $g_{\text{Cu-O}}(r)$, $g_{\text{Cu-Mg}}(r)$; the regularization parameters 5×10^{-4} ; number of iteration 99. All parameters have been tested in the model simulation until they provide solution to be free of procedure-introduced distortions. Final pPCFs have well distinguished first shell (Fig. 3). The more far peaks are present too, but as has been shown from model calculations there are no any guaranties in their coordinates. Also coordination numbers can not be obtained for three functions from one experimental data set. Hence the first interatomic distances have been obtained with a good accuracy. They have been compared to the nearest distances for MgO-based model and CuO data (Table 1).

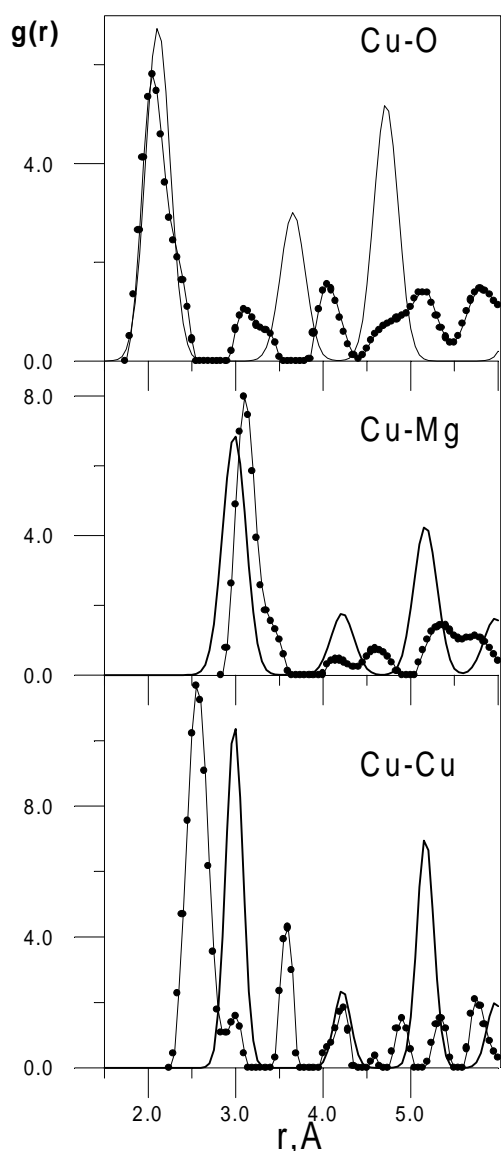


Figure 3
Pair partial correlation functions from Cu K-edge EXAFS experiment data (point-line) and from MgO-based model for $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ (solid line)

It is obvious, that the short range order of $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$ essentially differs from the short range order CuO, and from the hypothetical MgO-based structure:

- the first experimental interatomic distance Cu-Cu (2.56\AA) is not equal to the first interatomic distance Cu-Mg (3.11\AA),
- the distance Cu-Cu (Cu-Mg) for hypothetical lattice based on MgO ($a=4.219 \text{\AA}$) lies between experimentally obtained Cu-Cu and Cu-Mg distances and is equal to 2.98\AA ,
- the experimental Cu-O distance is close to the model distance for MgO-based model.

If it were really the pure MgO structure, the first and second result would not be obtained. Thus, on the basis of combine analysis of the X-ray scattering data and EXAFS it is possible to make a conclusion about *local distortions* of a NaCl crystal lattice around of Cu atoms. Concentration of Cu atoms is small, so the contribution of distorted regions is small too and does not effect the X-ray scattering spectrum. To determine other interatomic distances additional EXAFS experiments near Mg and O K-edges should be done. The average values of distances to be calculated and we suppose that it would be in a good agreement with lattice parameter from scattering data.

Table 1
First interatomic distances in $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$

	$r_{\text{Cu-Cu}}, \text{\AA}$	$r_{\text{Cu-O}}, \text{\AA}$	$r_{\text{Cu-Mg}}, \text{\AA}$
MgO-based model	2.98	2.11	2.98
Experimental results for $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{O}$	2.56 ± 0.01	2.05 ± 0.01	3.11 ± 0.02
CuO, experimental	2.92	1.97	—

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