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Structure determination of perovskites, high temperature superconductors and zeolites on the KSN-2 powder neutron diffractometer

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Abstract

The research activities at the Laboratory of Neutron Diffraction (Faculty of Nuclear Sciences and Physical Engineering CTU Prague) are focused on neutron scattering for solid state physics and materials science investigations. We have investigated a some promising materials, e.g. perovskites ($Pr_{1-x}K_xMnO_3$, $Pr_{1-x}Na_xMnO_3$ and $Pr_{1-x}Ca_xMnO_3$), high temperature superconductors (types Bi-Sr-Ca-Cu-O, Y-Ca-Ba-Cu-O) and zeolites (types Na-Y, Na-(H,D)Y, Na-X, Na-(H,D)X). Results obtained on the KSN-2 diffractometer by powder neutron diffraction method during last years are given.

1. Introduction

The crystalline structure of materials is fundamental to our understanding of their properties. In most cases it is necessary to determine the structural parameters or phase transition parameters of some perspective materials, which contain oxygen or hydrogen atoms among the heavy atoms. Then the neutron diffraction together with powder samples are advantageous to solve these problems. The powerful this application is pointed by means of the Rietveld analysis method for the neutron powder data treatment. Powder, or more correctly polycrystalline matter, is a common state of solid materials.

Therefore, our research activities are concentrated to the following ranges: crystallographic and magnetic structures, phase transformations, quantitative texture analysis and anisotropy of physical properties, residual stress analysis, in-situ investigations of phase transitions, kinetics of chemical reactions and texture developments. In addition to the experimental research programs, emphasis is placed on training of students in the use of neutron scattering techniques in the solid state physics and materials sciences.

Now, the brief description of our experimental devices and the summary of our results obtained during last years in the neutron diffraction research of the some technical interesting materials will be given.

2. Experimental

The neutron diffractometer KSN-2 is placed at the second horizontal beam tube of the research reactor LVR-15 in the Nuclear Research Institute near Prague. The KSN-2, a double axis powder diffractometer is intended to the structure and the texture experiments with polycrystalline samples and equipped with the auxiliary devices, e.g. programmed temperature control for cryostats and furnaces (closed cycle refrigenerator system mod. CP-62-ST/1, heater furnace mod. SVO-PT up 1000 K), texture goniometer TG-1, magnets. The KSN-2 is controlled by PCL 9812 computer and the different programs of the experiment control and data acquisition are available. This diffractometer offers good intensity with wavelengths in the range 0.095 to 0.141 nm and the best resolution value of $\Delta d/d = 0.001$ was reached in the region $d \sim 1.2 \div 0.07$ nm. At present time the KSN-2 diffractometer was upgraded and equipped by the bent Si(311) monochromator and the position-sensitive detector banks (P4 Reuter-Stokes). These reinstallations improve the recording time about 2.5 times and "in-situ" experiments are available. The diffraction patterns recorded are treated by Rietveld analysis method (code RIET-N, GSAS package, FULLPROF) and the complete structural parameters are determined.

3. Perovskites

Present interest in perovskites with Mn^{3+}/Mn^{4+} ions is stimulated by observation of electronic transitions which are related to the structure and magnetic ordering phenomena. The present communication deals with praseodymium based manganites substituted by monovalent cations.

The manganites $Pr_{1-x}Na_xMnO_3$ (x=0-0.2) have been synthetized and investigated by the neutron diffraction. All the systems show a perovskite structure with the tilt pattern of the Pbnm type. Similarly to related systems with substituted divalent alkali earths, the increasing monovalent sodium substitution generates charge carriers and changes gradually the magnetic groundstate from the layered A-type antiferromagnetism in $PrMnO_3$ (T_N=91 K) through canted arrangements for x~0.05 to the pure ferromagnetism for $0.10 \leq x \leq 0.15$ (T_C~125 K). An interesting feature is the detection of charge and orbital ordering ($T_{co} \sim 225$ K) followed by the "pseudo" CE type antiferromagnetic order (T_N= 175 K) in the compound with highest possible sodium concentration x=0.2 (the actual Mn^{3+}/ Mn^{4+} ratio in this sample was determined by the cerimetric titration to 64%:36%). The structure consists of two sublattices – one is composed of $Mn^{3+}O_6$ octahedra with a characteristic tetragonal elongation, which are oriented alternatively in the [110] and [1-10] directions; the other one is formed by the mixed valence $(Mn^{3+}/ Mn^{4+})O_6$ octahedra elongated along the [001] direction. As a result, the lattice metrics remains pseudocubic – a=5.446, b=5.430, $c/\sqrt{2}$=5.427 at 10 K, compared to a=5.450, b=5.437, $c/\sqrt{2}$=5.439 at 300 K. This is in distinction to the charge ordered manganites with ideal Mn^{3+}/ Mn^{4+} ratio of 50%:50% (e.g. $Pr_{0.5}Ca_{0.5}MnO_3$) where a marked tetragonal contraction along the b axis occurs. On the other hand, the structural and magnetic arrangement of $Pr_{0.8}Na_{0.2}MnO_3$ at low temperatures is analogous to the structure observed previously in the $Pr_{1-x}Ca_xMnO_3$ manganites with similar Mn^{3+}/ Mn^{4+} content (x~0.35) [1,2,3]. A novel finding on the present compound is a reorientation of the magnetic axis of the "pseudo" CE arrangement from the [001] to [100] direction below ~50 K. Charge and orbital ordering has been observed for the first time in rare earth manganites with monovalent substitution.

We conclude that the antiferromagnetic-ferromagnetic transition in the Mn^{3+}/Mn^{4+} perovskites occurs in a universal manner which does not depend on the kind of divalent or monovalent substitution. The observed behavior can be elucidated by an interplay of two main magnetic interactions, the superexchange and the double exchange [4].

4. High temperature superconductors

Among possible cationic substitutions in the $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_y$ superconductor, the partial replacement of Y^{2+} by Ca^{2+} has been found to be especially interesting. The heterovalent substitution changes the carrier concentration and may influence the charge transfer from the Cu-O chains to the conducting CuO_2 layers. Early studies have shown that such replacement was limited to about 25 % of yttrium and the critical temperature for the superconductivity in the orthorhombic samples (y~7) was lowered from 93 K for the calcium free compound to about 78 K for 20% of calcium [5,6]. For the latter compound, the superconductivity was detected also for highly reduced tetragonal samples (y=6.0-6.2). In order to investigate complexly the hole doping and the interlayer charge transfer also in the calcium substituted systems, we have undertaken simultaneous structural (X-ray and neutron diffraction), transport (electrical resistivity, thermoelectric power, Hall effect) and magnetic (AC susceptibility) studies on the $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_y$ ceramics within the whole accessible range of y. For five selected samples (y=6.13-6.89), a complete structural determination was achieved by neutron diffraction.

One of the important findings of the neutron diffraction performed on the $Y_{0.8}Ca_{0.2}Ba_2Cu_3Oy$ system is the linear increase of the c lattice parameter with decreasing oxygen content y. Similar behaviour was reported for $Y_{0.8}Ca_{0.2}Ba_2Cu_3Oy$ by Jorgensen et al. [7] and Cava et al. [8]. The comparison of our results with [7,8] suggests that in the whole region of the oxygen content the c parameter is shortened due to the Ca substitution roughly to about 0.0035 nm. They refer, however, to the helium temperature so that the comparison is not straightforward. The structure of the $Y_{0.8}Ca_{0.2}Ba_2Cu_3Oy$ type consists of a sequence of atomic layers, which play different roles in the carrier doping and charge transfer. Two copper cations per formula unit occupy sites Cu2 in the CuO_δ planes, considered as the main conducting part of the superconductor, and one copper cation occupies the Cu1 site in the CuO_2 plane of variable oxygen content (δ=7-y). In the orthorhombic region (y=7-6.4 for $Y_{0.8}Ca_{0.2}Ba_2Cu_3Oy$) the oxygen atoms in the CuO_2 plane are located preferentially in sites [0 1/2 0] and form characteristic Cu-O chains along the b-direction. For lower y values the structure is macroscopically tetragonal because the oxygen atoms are distributed equally over the (0,1/2, 0) and (1/2, 0, 0) sites or, for y=6 are eventually absent.

Complex studies of the $Y_{0.8}Ca_{0.2}Ba_2Cu_3Oy$ samples [9] with a large range of oxygen content y=6.89-6.03 have shown that the superconductivity occurs for $y \geq 6.4$. The investigation of the structure, electric transport and diamagnetism in $Y_{0.8}Ca_{0.2}Ba_2Cu_3Oy$ evidenced the important role of the oxygen ordering in the CuO_δ planes for the superconductivity. In contrary to the two superconducting plateaux found for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_y$ with Tc =90 and 60 K, three-plateau behaviour was observed and was identified with crystallographically different phases in the present system. First two plateaux correspond to phases with Tc of 80 K (6.89>y>6.75) and 50 K (6.75>y>6.50) and are associated with the Ortho I and II structures, characterized with infinite Cu-O chains. The third plateau corresponds to macroscopically tetragonal phase with Tc =25 K (6.50>y>6.40) and is possibly associated with formation of the Cu-O-Cu dimers. Moreover, each phase exhibits a distinct value of the room-temperature thermopower coefficient, which is preserved over the respective regions. All three superconducting phases in $Y_{0.8}Ca_{0.2}Ba_2Cu_3Oy$ exhibit sharp magnetic transitions with nearly complete diamagnetism

at low temperatures and a metallic-like electric conductivity in the normal state. The situation is dramatically changed at the transition to the non-superconducting region below y=6.4 where a sudden localization of carriers is observed.

5. Zeolites

Continuous interest in the structure investigation of zeolites is stimulated by their potential practical use in the chemical technology. Zeolites exhibiting regular structure which can be easily modified, are important candidates for this type catalyst and many laboratories try therefore to „tailor" zeolitic catalysts of the requested properties in oxygen atoms of the faujasite framerwork. Experimentally evidence of methoxy species on various zeolitic structures was given by ^{13}C NMR [10,11] recently. Spectroscopic methods [10] together with diffraction methods [11,12] are suitable and precise methods for characterization of the well defined synthetized structures. One of the most interesting knowledge which followed from neutron diffraction experiments on H, Na-Y zeolites was the fact that faujasite structure exhibits different crystallographic types of oxygen atoms (O(i), i=1-4). The same methods participate in the identification and location of the catalytic active sites - cations or protons [12], knowledge of which is extremely important for the better understanding of catalytic processes. Non-destructive testing methods, mainly neutron diffraction are used for the structure determination of these zeolite samples [13]. The fact that the powder materials can be measured in the stay which are similar considerations like in practice, is very important.

Results obtained from powder neutron diffraction pattern of the fundamental Na-Y sample at room temperature showed that the structural parameters of the framework atoms and cation distribution were in reasonable agreement with previous studies [14] (space group: Fd3m, lattice parameter a=2.4851(7) nm, R_{wp} = 6.92% and R_p =5.14%). Diffraction patterns (collected at 7 K) of chemisorbed samples were rather poorly fitted by an initial structure model involving just the framework and sodium ions. A difference Fourier maps showed that the chemisorbed methyl groups are connected to the O(1) oxygen preferentially and formed the bridging positions in the supercage of zeolite Y, where it interacts with O(1) (a six - ring bridging oxygen). If we introduce these locations of the methyl group CD_3 (or CH_3) respectively in 96(h) position of the Fd3m space group and during refinements C-O(1) and C-D (or C-H) distances are constrained for 0.1421 nm and 0.0957 nm (1,093 nm) respectively, than the reliability factors R_{wp} fell from 16.87% to 6.72% for the CD_3 and from 17.64% to 6.85% for CH_3 chemisorbed Na-Y samples, respectively. The conversion to NaI was estimated from the ^{13}C MAS NMR spectra.

It is clear that he population of cationic sites has been changed significantly after the chemisorption of methyl iodide. While the occupation of S_{II} in Na-Y without adsorbate was 32 Na^+ per unit cell (i.e. 100% occupation), after the chemisorption of CH_3I was found 19.6 (61%) and in case of CD_3I 21.4 (67%).

Rietveld analysis of the neutron diffraction data of NaX samples led to the complete set of the structural parameters for both the initial evacuated NaX sample and that with chemisorbed methyl species [15]. The structural analysis was treated in frame of Fd3 space group with a = 2.4976(7) nm, R_{wp} = 0.0516, R_p = 0.0468 (initial NaX sample) and with a = 2.4895(6) nm, R_{wp} = 0.0523, R_w = 0.0487 (chemisorbed NaX sample). For chemisorbed NaX sample we have determined the occupation numbers of cations and the location of CD_3 groups with the center in the position 96*g* (0.538, 0.130, 0.068). The occupation numbers of Na cations in chemisorbed NaX has been decreased for $S_{I'}$ and $S_{I''}$ in contrary to the increase for S_{III} in comparison with the initial NaX. S_{II} is practically fully occupied in both cases.

6. Conclusions

On the basis of our results we have proved that the KSN-2 diffractometer together with the Rietveld method of the analysis of powder neutron patterns is very important and powerfull tool for understanding the structure of the new interesting materials.

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