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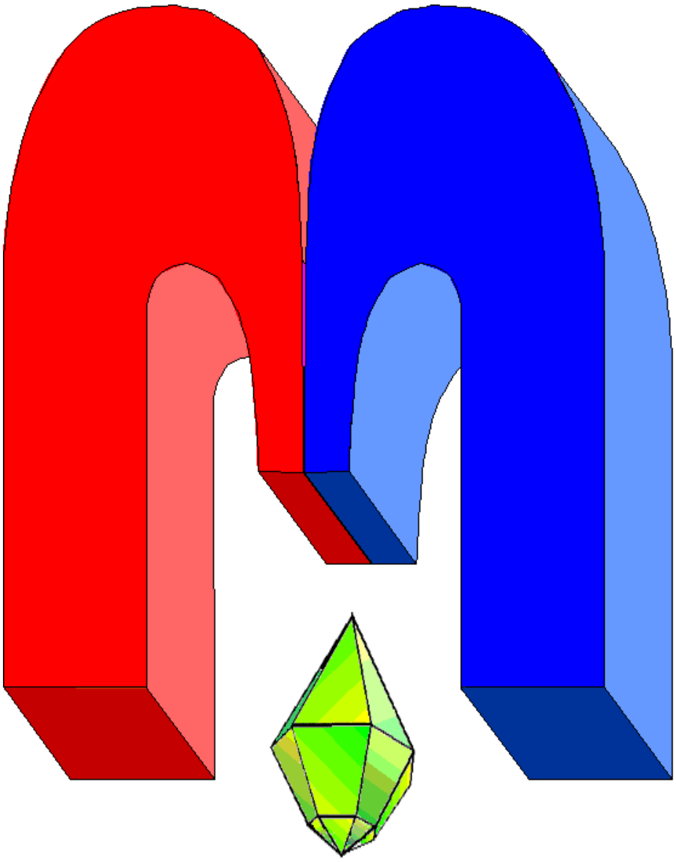

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[*] In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

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Thermally activated mobility of lithium ions in $Li_{1-x}CuSbO_4$ as studied by ^{7}Li NMR[†]

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The Li diffusion in $Li_{1-x}CuSbO_4$ with lithium deficiency $x = 0.02, 0.05, 0.07$ and 0.1 was studied by investigation of motional narrowing of the central ^{7}Li NMR line in the temperature range from 290 K to 470 K. The activation energy of hopping of lithium ions was determined from the temperature dependence of the NMR linewidth. The dependence of the obtained activation energy on the lithium content indicates the opening of motion channels in the crystals at x close to 0.1 due to the formation of free vacancies at the lithium position, which favors the thermally activated hopping of ions.

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1. Introduction

Intensive studies of low-dimensional transition metal oxides containing alkali metal ions, such as lithium and sodium, are currently very active, due to the prospects of their practical use as electrode materials for the manufacture of lithium-ion and sodium-ion batteries. Complex mixed oxides of alkali and transition metals exhibit a wide range of unusual physical properties, demonstrating the close connection of their crystal structure and magnetic, lattice and charge subsystems. Low dimensionality, in particular, is favorable to high ionic mobility due to the presence of channels for the movement of ions in such crystal structures [1]. NMR is a powerful method for studying internal structures, structural transformations, ion mobility and interfacial interactions in energy storage and conversion systems. NMR spectroscopy is distinguished from other research methods because it does not require direct contact with the test sample and does not include the use of aggressive media that destroy the test material. In addition, this local method allows one to selectively study the conductivity of interfaces and bulk materials, in particular, in powder samples; it provides data on the properties of the material, and not on grain boundaries. There are many different methods for studying ion mobility using nuclear magnetic resonance [2]. However, when working with transition metal oxides containing paramagnetic ions, it is very difficult to use such popular techniques as relaxometry or magic angle spinning due to the short relaxation time and large inhomogeneous spectral width caused by dipole interaction with paramagnetic ions. In this situation, the study of the temperature evolution of the width and shape of the NMR line becomes an effective method of characterization of ionic mobility [3]. With growth of temperature, the increasing hopping rate and, correspondingly, decreasing correlation time leads to the phenomenon of the so-called motion narrowing of the line. The study of the temperature dependence of the NMR line width allows one to obtain a number

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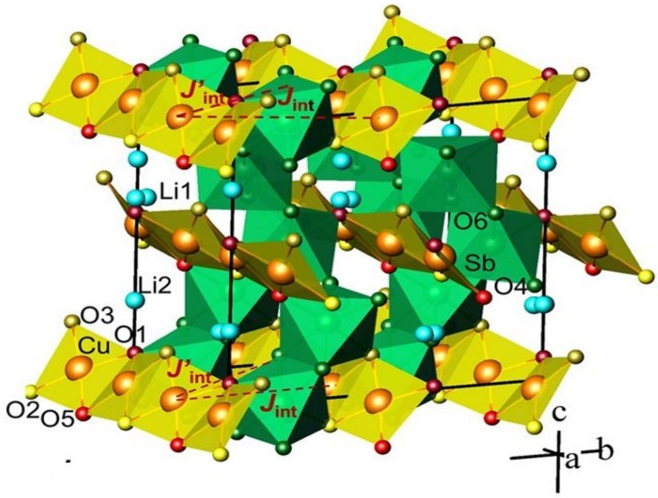

Figure 1. The crystal structure of $LiCuSbO_4$ [4].

of parameters characterizing the diffusion of ions in the crystal. The $LiCuSbO_4$ compound is interesting primarily for its low dimensional magnetism [4,5]. Due to the presence of strong Cu-spin frustrations, a successive change of nontrivial correlated phases with increasing magnetic field was found in it. The introduction of defects of various types is expected to have a significant effect on its magnetic and lattice characteristics. Moreover, such a type of defects as vacancies at the lithium position can also change the activation energy and ion mobility, as was observed in a number of other compounds [6–8]. In this work, ionic mobility in $LiCuSbO_4$ compound with various levels of lithium deficiency was investigated by nuclear magnetic resonance.

2. Materials and methods

The ^{7}Li nucleus has a spin $S = 3/2$ and has a quadrupole moment $^7Q = -0.04$ barn. The ^{7}Li NMR experiments were performed using a Redstone broadband pulsed spectrometer from Tecmag in the temperature range 290 – 470 K and in a magnetic field 0.725 T. A phase-cycling solid-echo pulse sequence consisting of two 90-degree pulses separated by short delay time was used for collecting the echo signal. Spectra were obtained by the Fourier transformation of the echo signal obtained at a frequency of 11.985 MHz. At relatively low temperatures (close to room temperature), when the line width was large enough, the shape of the spectrum was obtained by the spectrum was obtained as a combination of sections of lines measured at different frequency points with a sequential change in frequency. Polycrystalline sample of $Li_{1-x}CuSbO_4$ ($x = 0.02, 0.05, 0.07$ and 0.1) were prepared through solid-state reaction using stoichiometric mixture of dried Li_2CO_3, CuO and Sb_2O_5 [4]. In order to confirm the formation of the desired phase, all the samples were characterized by means of conventional powder X-ray diffraction.

3. Results and discussion

The crystal structure of the studied compound $LiCuSbO_4$ is shown in Fig. 1. Cu^{2+} ions are covalently bonded to four O^{2-} ions. The resulting non-planar CuO_4 plaquettes form chains oriented along the a-axis. The chains are interconnected by SbO_6 octahedra. The crystal structure contains 2 positions of lithium ions. The NMR response of each of their $S = 3/2$ nuclei consists of the main line and quadrupole satellites. Due to powder averaging and mainly due to inhomogeneous broadening, the structure of the spectrum is unresolved and it is recorded as one line with a low intensity pedestal. At room temperature, the line has a rather Gaussian shape; with increasing temperature, it acquires the Lorentzian form for all four samples.

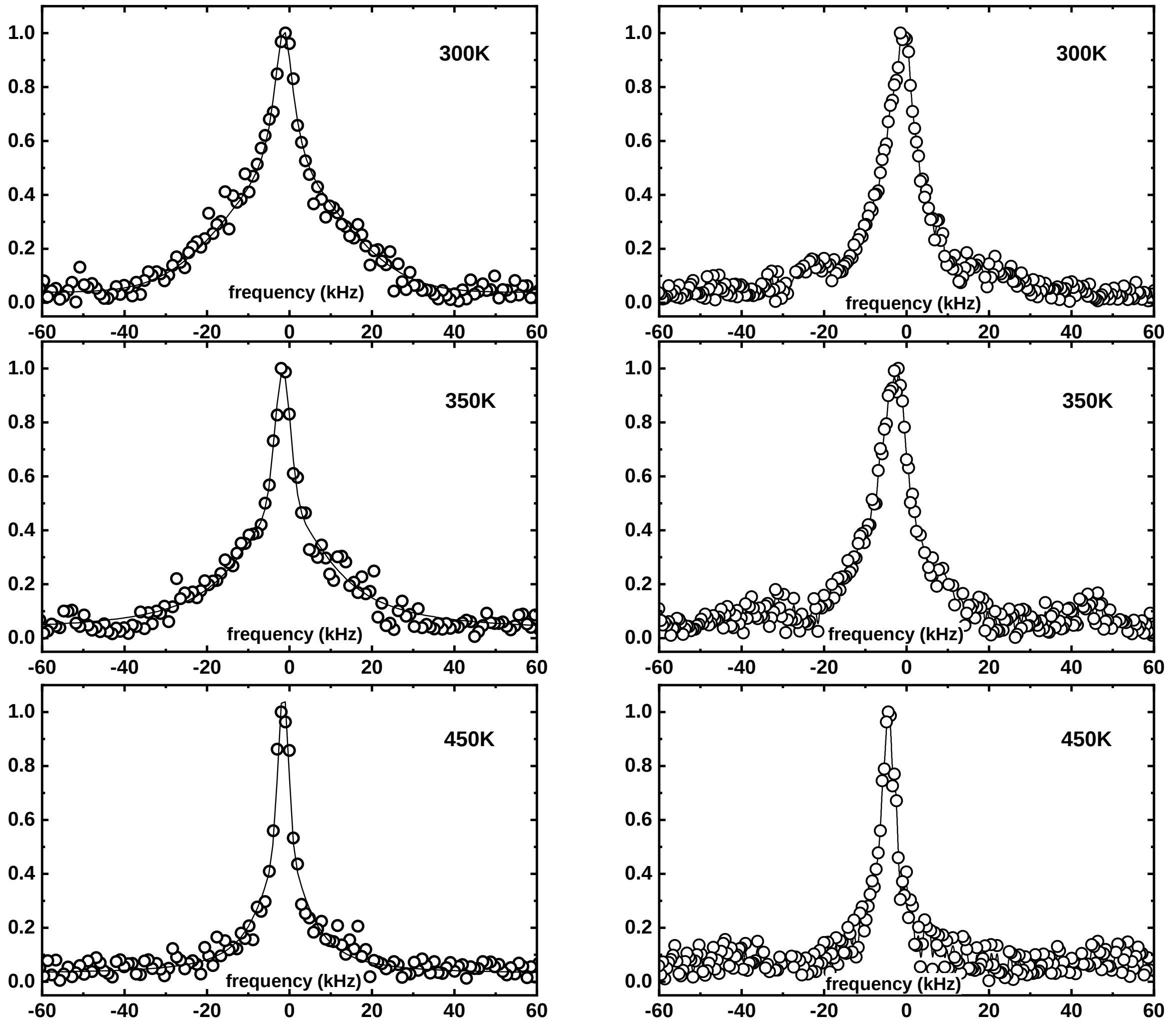

Figure 2. Normalized ^{7}Li NMR spectra of $Li_{1-x}CuSbO_4$ with $x = 0.02$ (left panel) and $x = 0.1$ (right panel) obtained at frequency 11.985 MHz at three characteristic temperatures 300, 350 and 450 K. Solid lines are drawn to guide the eye.

The line shape transformation for samples with the smallest and greatest lithium deficiency from this series is shown in Fig. 2. To conduct the analysis most correctly, we used further the line width at half maximum as a measured parameter. The temperature dependences of the line width for four samples shown in Fig. 3 demonstrate that at temperature above approximately 350 K, the line width decreases sharply and reaches a plateau at $T \approx 420$ K.

In the compounds with a high concentration of paramagnetic ions, the inhomogeneous line width, which reflects the distribution of local fields generated by the magnetic moments of these ions at the position of the nucleus, is usually determined by the temperature dependence of the magnetic susceptibility of ions. As can be seen from the data on the lash shift in the undoped compound, the bulk and local (Knight shift) susceptibility increases with decreasing temperature below 300 K. Our measurements of all four samples demonstrate that above 300 K the position of the line changed very weakly, almost within the measurement error. Since, as noted above, the line shift reflects the local susceptibility of the electronic subsystem at the position of the nucleus, we can conclude that at the temperatures of our experiments this contribution to the line width should not change significantly. Thus, the line width at a temperature of approximately 320 K is the so-called line width of the rigid lattice. Further narrowing of the line with increasing temperature is associated with an increase in the motion of Li. In this way, if the frequency of the

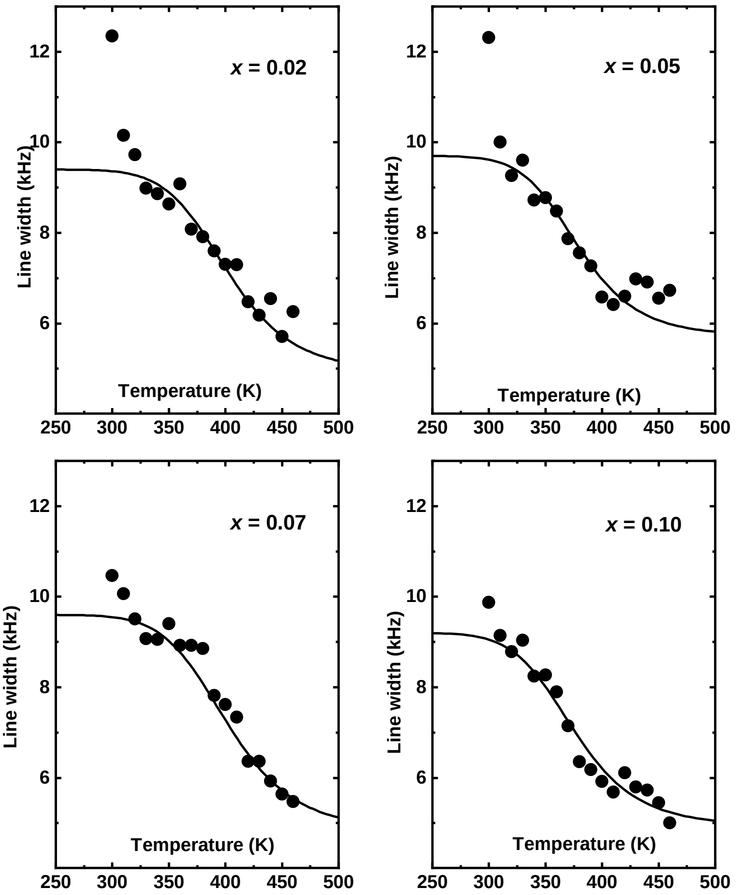

Figure 3. Temperature dependences of the NMR line width at half maximum for samples with various lithium deficiencies. Solid line is approximation according to Eq. (2).

ion jumps exceeds the inhomogeneous broadening caused by the interaction with paramagnetic ions and other lithium nuclei, the local fields in the nuclei position become more and more averaged. This leads to a narrowing of the line width down to $\approx 5-6\,\mathrm{kHz}$ at T reaching 450 K. The line width at these temperatures is determined by processes that are not averaged by the diffusion of ions, primarily the inhomogeneity of the external magnetic field on the sample length. The narrowing process is accompanied by a change in the shape line from Gaussian to Lorentzian.

The ion hopping frequency can be characterized by the correlation time, which varies with temperature in an activation manner according to the Arrhenius law

$$\tau_{\mathrm{hop}} = \tau_0 \exp(E_\mathrm{a}/k_\mathrm{B}T), \tag{1}$$

where E_a is the activation energy, k_B is the Boltzmann constant, τ_0 is determined by the characteristic frequencies of local jumps of the ion at high temperatures. The temperature dependence of the line width, thus, allows one to estimate the activation energy of Li diffusion. There are several ways to determine the value of activation energy [9–11]. For a very rough estimation of the activation energy, one can use the empirical Waugh-Fedin formula $E_\mathrm{a}(\mathrm{eV}) = 1.617 \cdot 10^{-3} \cdot T_\mathrm{c}(\mathrm{K})$, where T_c is the onset temperature of motional narrowing. Assuming $T_\mathrm{c} = 320\,\mathrm{K}$ we get $E_\mathrm{a} = 0.517\,\mathrm{eV}$. For more precise determination of activation energy of Li-ion motion in samples with different lithium content we use the function given in ref. [10]:

$$\Delta\nu(T) = \frac{\Delta\nu_\mathrm{R}}{1 + \left(\frac{\Delta\nu_\mathrm{R}}{B} - 1\right)\exp\left(-\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)} + D, \tag{2}$$

where $\Delta\nu(T)$ is the line width at half maximum, $\Delta\nu_\mathrm{R}$ is the line width for rigid lattice, E_a

is the activation energy, B and D relate respectively to the linewidth of nuclei of thermally activated ions and temperature-independent line width caused, e.g., by the inhomogeneity of the external static magnetic field. The fitting curves are presented in Fig. 3. The obtained fitting parameters $\Delta\nu_{\mathrm{R}}$, B and D were of the same order of magnitude as those used in ref. [12]. The dependence of the obtained activation energy of lithium ions on the lithium content in the samples of $\mathrm{Li}_{1-x}\mathrm{CuSbO}_4$ is shown in Fig. 4. The obtained values are consistent with a rough Waugh–Fedin estimation. At a relatively small deficiency of lithium the activation energy changes slightly, while at x of the order of 0.1 a clear decrease of E_{a} is observed. This, apparently, indicates the opening of motion channels in the crystal due to the formation of free vacancies at the lithium position, which favors the thermally activated hopping of ions.

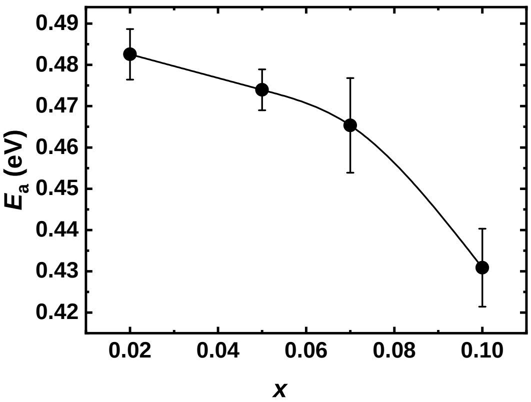

Figure 4. The dependence of the lithium ions activation energy E_{a} on the lithium deficiency. Solid line is drawn to guide the eye.

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