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Electronic State of Vanadium Ions in $Li_{1+x}V_3O_8$ According to EPR Spectroscopy

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EPR spectroscopy is used to study the electronic state of vanadium ions in HT- and LT-$Li_{1+x}V_3O_8$. It is shown that in both cases the EPR spectra observed are attributed to vanadyl VO^{2+} ions (localized electron centers) with weak exchange interaction. The other type of registered electrons is characterized by larger mobility through a few V^{5+} ions, i.e., by a higher degree of delocalization (electron gas). Based on the analysis of the temperature dependence of the EPR line width, it is stated that the exchange interaction between localized electron centers proceeds through electron gas (C–S–C relaxation). It is found that HT-$Li_{1+x}V_3O_8$ differs from LT-$Li_{1+x}V_3O_8$ by the sloping form of its spectrum at $g_{\parallel}$ range connected with two types of VO^{2+} ions different in the direction of the crystal field axis corresponding to a short $V{=}O^{2+}$ bond. © 2002 Elsevier Science (USA)

Key Words: **lithium–vanadium oxide; EPR; vanadyl ions; C–S–C relaxation.**

INTRODUCTION

$Li_{1+x}V_3O_8$ is a bronze-type compound in the V_2O_5–$LiVO_3$ system. Some of the V^{5+} ions in it are reduced to V^{4+} (1, 2). $Li_{1+x}V_3O_8$ crystallizes in a monoclinic system. The structure of $Li_{1+x}V_3O_8$ is closely related to that of V_6O_{13} ($V_{2n}O_{5n-2}$). It consists of double and single zigzag octahedral strings arranged so as to provide interlayer places (tetrahedral and octahedral) for lithium ions. It is achieved by expanding the framework of vanadium polyhedra. Wadsley (1) differentiated three types of vanadyl groups (V=O) in the lattice of $Li_{1+x}V_3O_8$ with bond lengths of 1.59, 1.60, and 1.64 Å. Three bands in the 900–1000 cm^{-1} range observed in the IR spectra of $Li_{1+x}V_3O_8$ were assigned by Kera (3) to three unequivalent V=O groups compared to the single vibration band at 1022 cm^{-1} in the spectrum of pure V_2O_5 with only one V=O bond (1.56 Å) in its structure. The shift of the bands toward the low-frequency region in the spectrum of $Li_{1+x}V_3O_8$, probably, is determined by the presence of lithium ions in interlayer positions.

In recent years $Li_{1+x}V_3O_8$ has received a good deal of attention as a cathode material for rechargeable lithium batteries because of its high capacity, facile preparation, and stability in air (4–6). $Li_{1+x}V_3O_8$ is usually prepared either by high-temperature methods (e.g., by melting of a mixture of Li_2CO_3 and V_2O_5) (4) or by low-temperature ones (e.g., by codissolution of lithium and vanadium compounds) (5, 6). It was shown (5, 6) that the electrochemical performance of $Li_{1+x}V_3O_8$, such as its capacity, rate stability, and cyclability, is strongly influenced by its preparation method. Studying the reason for the different properties of LT-$Li_{1+x}V_3O_8$ as compared with HT-$Li_{1+x}V_3O_8$, some authors (5) suggested that it consists of a lower degree of crystallinity, a strained V_3O_8 layer, a different crystallite orientation, and a higher specific surface area. Other authors (6) pointed to the absence of long-range ordering, the enhanced flexibility of the unit cell, and the increased degree of isotropy, reducing the length of the pathways through which Li^+ ions diffuse.

Because some of the V^{5+} ions in $Li_{1+x}V_3O_8$ are reduced to V^{4+}, one can also suppose that HT- and LT-$Li_{1+x}V_3O_8$ differ from each other by the concentration and electronic state of V^{4+} ions. Moreover, according to (2), $Li_{1+x}V_3O_8$ is characterized by oxygen nonstoichiometry dependent on the conditions of synthesis. Wickham proposed to use the formula $Li^{+}_{1+x}V^{4+}_{y}V^{5+}_{3-y}O_{8-y/2+x/2}$. Note that oxygen nonstoichiometry can influence the interaction between V^{4+} ions.

The aim of the present study was to investigate the electronic state of V^{4+} ions in HT- and LT-$Li_{1+x}V_3O_8$ by EPR spectroscopy.

EXPERIMENTAL

Li_2CO_3 and V_2O_5 (qualification "pure for analysis") were used as initial reagents. The molar ratio Li/V in the starting

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mixtures corresponded to a stoichiometry of $Li_{1.07}V_3O_8$. HT-$Li_{1.07}V_3O_8$ was prepared by melting of the mixture of V_2O_5 with Li_2CO_3 at 680°C, and LT was prepared by dissolution of Li_2CO_3 with NH_4VO_3 in boiling water with subsequent evaporation of solution and heating of the precursor at 350°C in the air. Analogous methods were used for preparation of HT- and LT-$Li_{1+x}V_3O_8$ in (4) and (5), respectively.

EPR spectra were recorded by using a Bruker EPR spectrometer ($\lambda = 3$ cm) at 293 and 77 K. The error of g-factor determination corresponded to ± 0.003. Integral intensity was measured by double integration in comparison with the standard and with an error of about 30%.

X-ray patterns were obtained by using a DRON-3.0 diffractometer (Cu$K\alpha$ radiation) and IR spectra by using a Bruker IR spectrometer (pellets with CsI). Chemical analysis was performed by using an atomic emission spectrometer with ICP. The concentration of V^{4+} ions was analyzed by the method described in (2).

RESULTS AND DISCUSSION

According to chemical analysis, the Li/V ratio in the $Li_{1+x}V_3O_8$ samples as prepared corresponds to the initial one within the error of the measurements. The concentration of V^{4+} ions in HT- and LT-$Li_{1+x}V_3O_8$ is equal to 6.15 and 7.95 mass %, respectively. Thus, the chemical formula of HT- and LT-$Li_{1+x}V_3O_8$ can be represented as follows: $Li_{1.07}V^{4+}_{0.18}V^{5+}_{2.82}O_{7.94}$ for HT and $Li_{1.07}V^{4+}_{0.24}V^{5+}_{2.76}O_{7.92}$ for LT sample, pointing to a relatively equal lack of oxygen.

Figure 1 shows X-ray patterns of HT- and LT-$Li_{1+x}V_3O_8$ as prepared. They are similar to those obtained in (5). The reflections of LT-$Li_{1+x}V_3O_8$ are less intensive compared to HT-$Li_{1+x}V_3O_8$. The most profound difference is in the relative intensity of the (100) peak which is much stronger for the HT sample. The authors of (5, 6) supposed that this may be attributed to the different orientation of crystallites in the powdered samples since in the powder XRD experiments of HT-$Li_{1+x}V_3O_8$ with larger crystallites the preferred orientation is not always avoided.

The phase analysis of XRD patterns of the samples as prepared was based on the data published by ASTM. The majority of reflections for both samples corresponds to $LiV_3O_{7.9}$ (N 18-754); nevertheless, some reflections can be assigned to LiV_3O_8 (N 35–437). A more detailed analysis of the crystal structure of the samples was beyond the scope of the present study.

While analyzing X-ray patterns, we could not establish unambiguously the presence or absence of other lithium–vanadium bronzes as an admixture. But EPR data (see below) have confirmed that they were absent. Some weak reflections in X-ray patterns of $Li_{1+x}V_3O_8$ samples as prepared can be assigned to $LiVO_3$. Note that some authors (7) succeeded in the preparation of homogeneous $Li_{1+x}V_3O_8$ in the V_2O_5–$LiVO_3$ system when using low cooling. In contrast, a mixture of $Li_{1+x}V_3O_8$, β-$Li_xV_2O_5$, and $LiVO_3$ was formed with fast cooling.[2]

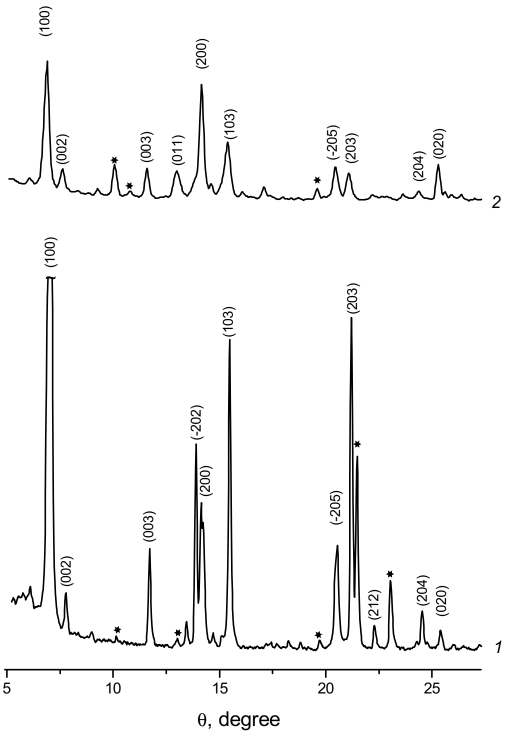

FIG. 1. X-ray patterns of HT- (1) and LT-$Li_{1+x}V_3O_8$ (2). Reflections with *hkl* indexes correspond to $LiV_3O_{7.9}$ (ASTM N 18-754) and with V $*$ to LiV_3O_8 (ASTM N 35-437).

Unlike the X-ray data, the IR spectra of HT- and LT-$Li_{1+x}V_3O_8$ are similar to each other (Fig. 2). Whereas for pure V_2O_5 the absorption band corresponding to stretching vibrations of double vanadyl bonds ν(V=O) is observed at 1020 cm^{-1} (curve 1), for HT- and LT-$Li_{1+x}V_3O_8$ it is shifted to the 900–1000 cm^{-1} range. The spectra of the $Li_{1+x}V_3O_8$ samples have three bands at 920, 950, and 995 cm^{-1} which were assigned in (3) to three different double bonds.

EPR signals observed for HT- and LT-$Li_{1+x}V_3O_8$ are attributed to V^{4+} ions (d^1 electron configuration). The spectrum of LT-$Li_{1+x}V_3O_8$ at 77 K (Fig. 3) is represented by a single line without hyperfine structure (HFS). It is characterized by distinct axial anisotropy of the g-factor

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[2] According to IR and EPR data, LT-$Li_{1+x}V_3O_8$ was also free of $(NH_4)_{1+x}V_3O_8$ impurities. In IR spectra of this sample the bands corresponding to NH_4^+ ions vibrations were absent. Moreover, in our EPR study we observed lines corresponding only to the vanadium–oxide bond, namely the vanadyl bond $V{=}O^{2+}$ (see later). If $(NH_4)_{1+x}V_3O_8$ is formed, we should observe vanadium–NH_4^+ ions bond with larger g-factors as NH_4^+ ions form covalent bond with cations only.

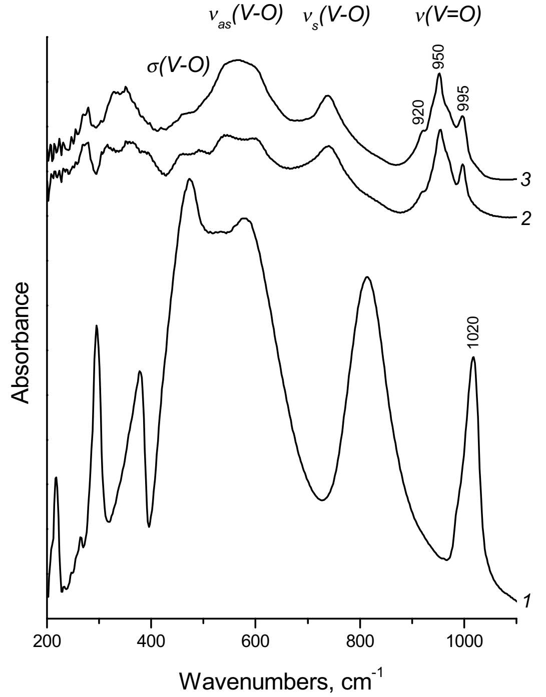

FIG. 2. IR spectra of initial V_2O_5 (1), HT- (2), and LT-$Li_{1+x}V_3O_8$ (3).

and belongs to exchanged V^{4+} ions.[3] The calculated parameters of the spectrum are equal to $g_{\parallel} = 1.94$ and $g_{\perp} = 1.96$. At 293 K the spectrum is broadened; the integral intensity obeys the Curie law at 77–293 K. It evidences the absence of lithium–vanadium bronzes $Li_xV_2O_5$ in the sample since it is known (7) that the mobility of unpaired electrons in these bronzes is activated. This should lead to significant broadening of their EPR spectra at 300 K. The EPR spectrum of HT-$Li_{1+x}V_3O_8$ is almost the same but with weaker anisotropy and the sloping form in the $g_{\parallel}$-range. The line width of this sample is changed from 50 G at 77 K to 88 G at 293 K. The form of the spectrum allows us to determine confidently only $g_{\perp}$ ($g_{\perp} = 1.96$), but not $g_{\parallel}$ since the axes of g-factors of exchanged V^{4+} ions are swung to each other, probably thanks to a disturbance of the direction of the axial component of the crystal field. It can be connected with the strong influence of lithium ions located in the coordination sphere of vanadyl ions VO^{2+}. Note that in the case of LT-$Li_{1+x}V_3O_8$ all axes of $g_{\parallel}$ coincide with the direction of the vanadyl bond V=O. The integral intensity of spectra for both samples corresponds to the amount of V^{4+} ions in $Li_{1.07}V_3O_8$ within the error of EPR measurements ($\sim$ 10 mass %).

The peculiarities of the electronic state of vanadium ions with vanadyl bonds in numerous vanadyl complexes $V^{4+}OL_2$ (where L is a ligand) were successfully studied by EPR spectroscopy (8). Ioffe and Patrina have observed vanadyl ions in V_2O_5 monocrystals doped by single-charged cations (Li^+, Na^+, K^+, Cu^+) (9). The unique property of unpaired electrons has been found, i.e., the existence of their mobility through a few (two, four, or more) V^{5+} ions. This process was accompanied by multiple changing of the HFS constant of ^{51}V nuclei from A_0 for one $V^{5+} + e(V^{4+})$ ion to $A_0/2$ for $2V^{5+} + e(V_2^{9+})$ ions and further to A_0/n ($n \to \infty$), where n is the number of ^{51}V nuclei (according to Ioffe, $I = 0$). It has been shown that delocalization does not depend on the measurement temperature.

EPR spectra of V^{4+} ions without HFS were observed for different lithium–vanadium bronzes, e.g., for $Li_xV_2O_5$ and

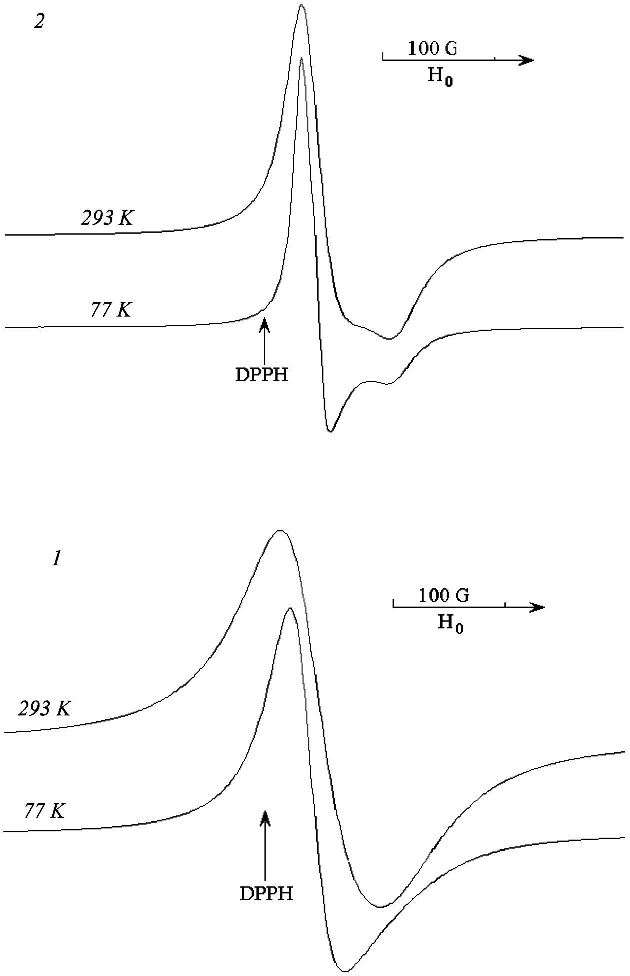

FIG. 3. EPR spectra of HT- (1) and LT-$Li_{1+x}V_3O_8$ (2) at 77 and 293 K.

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[3] The observed EPR spectra correspond to tetragonally pressed octahedra. It is too complicated to distinguish the unequivalency of the V–O distance in the equatorial plane in this case. Therefore, the term "pressed octahedron" is better to use than "distorted trigonal bypyramid," according to Wadsley (1).

$Li_{2+2x}V_6O_{16}$ prepared by thermal synthesis (7, 10) and $Li_xV_2O_5$ and $Li_xV_6O_{13}$ prepared by intercalation of lithium ions in the reaction of *n*-butyl lithium with V_2O_5 and V_6O_{13} (11). In some cases the authors registered narrow anisotropic lines, but this phenomenon was not discussed in the papers. The authors did not determine the values of $g_{\parallel}$ and $g_{\perp}$ for observed spectra which allow us to discuss the peculiarities of the vanadyl bond. No detailed study of $Li_{1+x}V_3O_8$ by EPR spectroscopy has been found in the literature.

The analysis of parameters of the experimental EPR spectra of HT- and LT-$Li_{1+x}V_3O_8$ observed in the present study and their changing with the measurement temperature leads to the following conclusions: the anisotropic spectra registered for both samples are attributed to vanadyl ions $V{=}O^{2+}$. It follows from the value of the *g*-factor and the time of spin–latice relaxation T_1.

The value of $g_{\perp}$ ($g_{\perp} = 1.96$) is typical for vanadyl complexes VOL_2 (where *L* is a ligand) (8). According to the MO LCAO model, these complexes are characterized by strong covalency of the V=O bond. This model considers the existence of a noticeable covalency of the out-of-plane π-bond of the atomic orbitals d_{xz}, d_{yz} of the V^{4+} ion with the oxygen *p*-orbital of vanadyl bond. Taking into account the sharp decrease of the constant of the spin–orbital bond in vanadyl ions VO^{2+}, as compared with free V^{4+} ions, it leads to $g_{\perp} = 1.98$–1.99 for most vanadyl ions. At the same time, for vanadyl complexes $VO^{2+}L_2$ with oxygen-containing ligands *L*, $g_{\perp}$ is slightly less and equal to 1.96–1.97.

Such *g*-factors are also observed for vanadium oxide compounds. For example, in the case of vanadium-doped rutile TiO_2, when V^{4+} ions are located at the interstitial positions *I*, strongly pressed octahedra with two short Ti–O bonds (1.6 Å) are observed (12). As a result, the parameters of EPR spectra are typical for vanadyl ions VO^{2+} ($g_{\parallel} = 1.94$, $g_{\perp} = 1.97$). The *g*-factor of isolated VO^{2+} ions in the V_2O_5 monocrystals doped by lithium are of the same order too: $g_{\parallel} = 1.92$, $g_{\perp} = 1.98$ (9).

In the case of a perfect octahedral oxygen environment, when the vanadyl bond is absent, $g_{\perp}$ sharply decreases. It follows from the crystal field theory for V^{4+} ions in octahedra and is confirmed by numerous experiments for d^1 ions in oxygen-containing systems (13). For example, V^{4+} ions in the substitutional positions *S* of rutile are located in practically perfect octahedra with a Ti–O distance of 1.98 Å (two bonds) and 1.94 Å (four bonds). Considering the second coordination sphere, the crystal field surrounding V^{4+} ions corresponds to a weakly pressed octahedron. In this case, $g_{\perp} = 1.92$ due to the weak covalency of the V^{4+} ion bond with oxygen ligands in the *S* positions (12). This is noticeably less than the $g_{\perp}$ values for vanadyl complexes.

It is known that spectra of V^{4+} ions, located in a perfect oxygen octahedron, are characterized by a short time of spin–lattice relaxation T_1 owing to the weak splitting Δ of the t_{2g} term of d^1 ions ($\Delta H \sim 1/T_1$). For example, for V^{4+} ions in the substitutional positions *S* of rutile (practically perfect octahedra) (12, 13), $T_1^{-1} \sim \Delta^n$ according to different physical models. This leads to a sharp increase of the line width as the measurement temperature increases. As a result, spectra of V^{4+} ions in the substitutional positions of rutile are observed at 77 K and lower temperature only. In contrast, due to the strong splitting of the t_{2g} term in the case of a pressed octahedron, the time of spin–lattice relaxation T_1 becomes longer, and EPR spectra of V^{4+} ions in *I* positions are also observed at room temperature. It is typical for vanadyl complexes, too (12, 13).

Thus, experimental spectra of HT- and LT-$Li_{1+x}V_3O_8$ can be assigned to vanadyl ions $V^{4+}{=}O$. This indicates that though three short V–O bonds are observed in the structure of $Li_{1+x}V_3O_8$ by X-ray diffraction (1) and IR spectroscopy (3), probably only one of them is really a vanadyl bond $V^{4+}{=}O$. The two others can be attributed to V^{5+}–O bonds, likely possessing some degree of covalency as a result of partial delocalization of electrons of oxygen ions through some neighboring V^{5+} ions. As mentioned above, it is really observed in partially reduced V_2O_5 (9). On the basis of this assumption, one can explain a sharp decrease of the vibration frequencies of the vanadyl bonds in the IR spectra of the $Li_{1+x}V_3O_8$ samples, compared to V_2O_5, by the influence of Li^+ ions on oxygen anions of VO^{2+} groups through a noticeable increase of their effective mass and a corresponding decrease of their vibration frequency.

The observed narrowing of EPR spectra, up to the appearance of a narrow anisotropic signal at lower temperature, is impossible to connect with small t_{2g} term splitting since vanadyl ions are characterized by a large splitting of the t_{2g} term. Most probably, the temperature dependence of the line width can be explained by the model, considering the influence of interaction of localized electrons (V^{4+} ions, in this case) with electron gas, formed from another part of vanadium ions (*C*–*S* relaxation) (14).

Figure 4 demonstrates two possible models which concern the influence of electron gas *S* on relaxation character-

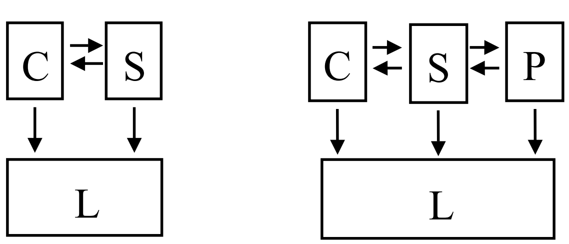

FIG. 4. Schemes of *C*–*S* (1) and *C*–*S*–*P* (2) relaxation: *C*, paramagnetic ion; *S*, electron gas; *P*, impurity; *L*, lattice (17, 18).

istics of localized electrons *C*: *C–S* and *C–S–P* relaxation. These models describe the peculiarities of EPR spectra in the systems comprised of localized electrons *C* (long relaxation time T_1) and electron gas *S* (short relaxation time T_1) considering their interaction with the lattice *L*. According to the first model, localized centers interact with electron gas through an exchange mechanism. Electron gas changes the time of relaxation of localized unpaired electrons through exchange interaction ($W \sim J \cdot S_c \cdot S_s$). This leads to a dependence of ΔH on temperature. One well-known example of electron gas in oxide structures is V_2O_4 which undergoes a dielectric–metal Mott transition (15). Doping of V_2O_4 by Fe^{3+} ions is accompanied by a sharp broadening of the EPR spectra of Fe^{3+} ions around the dielectric–metal transition temperature of V_2O_4 with increasing temperature (16).

The second model represents a more common case and was well studied long ago (so-called “bottle-neck mechanism”) (17, 18). It describes the energy exchange between localized *C* and *P* centers through electron gas and defines the dependence of the EPR line width of the localized center upon the value of exchange integral and the amount of conductive electrons, and the temperature. If electron gas is two-dimensional due to formation of fragments of the oxides with dielectric–metal transition (e.g., V_2O_4, V_6O_{13}, $Li_xV_2O_5$), the EPR spectrum should be broadened as the temperature increases $\Delta H \sim T$ due to relaxation of an unpaired electron with the lattice by means of electron gas. This corresponds to the experimental results (14). Such a dependence is observed when the exchange integral *J* between unpaired electrons and electron gas is noticeable.

Hereby, the model described above supposes the fragments with electron gas to be built into the structure of $Li_{1+x}V_3O_8$ with localized electrons as, for example, occurs in the case of formation of a shift structure in reduced rutile (19). Probably, the observed experimental spectra of $Li_{1+x}V_3O_8$ can be explained by weak exchange energy between localized centers through electron gas (*C–S–C* relaxation), where *C* are V^{4+} ions with localized electrons and *S* is an electron gas, which is formed from V^{4+} ions with completely delocalized electrons. The presence of a small exchange integral *J* leads to the disappearance of HFS, but the Curie law in the 77–293 K range is not disturbed thanks to the low value of the Neel temperature for the weak exchange interaction. Evidently, the Curie law for these samples can be disturbed at helium temperature only.

Thus, the observed EPR spectra of the $Li_{1+x}V_3O_8$ samples evidence the presence of two types of homogeneous ions; localized VO^{2+} ions and delocalized ones entering into the composition of different structural fragments. The presence of an exchange interaction of localized vanadyl ions through the electron gas testifies to the absence of phase boundaries between these fragments. This is close to the case of shift structures observed in reduced rutile (19).

To conclude, the difference between the spectra of HT- and LT-$Li_{1+x}V_3O_8$ was found to consist in the sloping form of the line at the $g_{\parallel}$ range without a clear peak at the $g_{\parallel}$ range for HT-$Li_{1+x}V_3O_8$. Note that such an uncommon form of EPR spectra was observed for exchanged Cu^{2+} ions in dimers, when the axes of symmetry of crystal field of ions in these pairs are swung to each other at a definite angle (20). Probably, in our case, the sloping form of the spectrum of HT-$Li_{1+x}V_3O_8$ can also be interpreted as a spectrum of the system of exchanged localized $V{=}O^{2+}$ ions of two types which differ from each other by the direction of the crystal field axis corresponding to a short $V{=}O^{2+}$ bond. Probably, the reason for the change of the crystal field axis for about 50% of the $V{=}O^{2+}$ ions lies in the presence of Li^+ ions in their coordination sphere, which influence the symmetry of the crystal field around the $V{=}O^{2+}$ ions.

CONCLUSION

Thus, it is shown that EPR spectroscopy data shed light on the electronic state of V^{4+} ions in $Li_{1+x}V_3O_8$ prepared by high- and low-temperature methods. In both cases, the presence of vanadyl VO^{2+} ions (localized electron centers) with weak exchange interactions has been stated. In contrast to the existing opinion on the presence of three vanadyl bonds in the $Li_{1+x}V_3O_8$ structure based on X-ray diffraction and IR spectroscopy data, it has been found that all vanadyl ions observed by EPR belong to one type with an equal V–O distance and a high degree of covalency. Another type of registered electrons is characterized by larger mobility through some V^{5+} ions, i.e., a higher degree of delocalization (electron gas). For the first time, the presence of exchange interaction between localized electron centers in $Li_{1+x}V_3O_8$ is defined, which proceeds through electron gas (*C–S–C* relaxation). It was found that HT-$Li_{1+x}V_3O_8$ differs from LT-$Li_{1+x}V_3O_8$ by the more noticeable influence of lithium ions on the symmetry of the crystal field of V=O ions as a result of different crystal structures. It demands new detailed investigations on the crystal structure of $Li_{1+x}V_3O_8$ prepared at different temperatures.

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