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Intramolecular and Lattice Dynamics in $V_{6-n}^{IV}V_n^V O_7(OCH_3)_{12}$ Crystal

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Multi-nuclear mixed-valence clusters $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ were studied by X-band EPR in the temperature range 4.2–300 K. An isotropic exchange interactions between four V^{IV} ions with individual spin $S_i = 1/2$ determine the energy levels structure of the compound with the total spin states $S = 0, 1$, and 2, which are doubled and split due to the extra electron transfer. The spin-Hamiltonian approach was used for the analysis of the temperature dependences of the EPR spectra parameters and the cluster dynamics. Two types of the electron transfer are assumed: the single jump transfer leading to the splitting of the total spin states by intervals comparable in magnitude with the exchange parameter $J \approx 100–150 \text{ cm}^{-1}$ and the double jump one resulting in dynamics. The dependence of the transition rates ν_{tr} on the energy of the total spin states was observed. In particular, in the range 300–220 K the $\nu_{\text{tr}} \approx 0.7 \times 10^{10} \text{ cm}^{-1}$ and below 180 K the $\nu_{\text{tr}} \approx 1 \times 10^{10} \text{ cm}^{-1}$ was estimated. The g -factors of the spin states were shown to depend on the values of the intermediate spins. A phase transition in the T -range 210–180 K leading to the change in the initial V^{IV} ions localization was discovered.

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1. Introduction

The magnetic properties of polynuclear clusters containing structurally equivalent transition metal ions in different oxidation states are determined by two basic phenomena, namely exchange interactions and electron transfer. The

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possibility of different distribution of oxidation states within a cluster leads to additional degeneracy of spin multiplets formed by Heisenberg–Dirac–van Vleck (HDVV) exchange interactions. The electron transfer partly or completely removes this degeneracy. The resulting energy spectrum depends on the cluster geometry and the number of mobile electrons, and in any case strongly differs from the original HDVV picture. For clusters with delocalized electrons two physically different cases can be distinguished. The first one concerns systems with “excess” electrons migrating between paramagnetic cores, leading to well known double exchange interaction [1, 2]. These phenomena were analyzed especially in application to mixed-valence iron–sulphur clusters [3, 4]. Another situation arises in systems with spinless ionic cores. The most known example of such systems is given by reduced (so called “blue”) polyoxometalates. These metal–oxygen anionic clusters with metal ions in d^0 electronic configuration can accommodate several excess, usually strongly delocalized, electrons. As it has been shown by several theoretical studies, if two electrons reduce a polyoxoanion, the delocalization leads to a strong stabilization of singlet spin state [5–9]. This stabilization is due to the filling of the lowest non-degenerate delocalized molecular orbital by two electrons. However, highly symmetrical polyoxoanions give rise to vacant degenerate molecular orbitals, which should be populated by supplementary reducing electrons [6, 7]. The analysis of magnetic properties of such systems, where a purely delocalized description is further complicated by the presence of exchange interactions between unpaired electrons, presents a challenge for future theoretical and experimental studies.

We studied the magnetic behaviour and intramolecular dynamics of the mixed-valence cluster $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ by electron paramagnetic resonance (EPR). We succeeded in getting information on the unpaired electron transfers; the energies of the total spin states and transitions between the possible configurations of V^{IV} ions. In this compound a phase transition was discovered.

2. Experimental results

The crystal structure of the $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ compound belongs to the $P2_1/n$ space group with four magnetically non-equivalent cluster-molecules in the unit cell [10, 11]. In each mixed valent cluster $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ the six vanadium nuclei surround an oxoanion forming a slightly distorted octahedron. The

TABLE

V–O bond lengths [\AA] in $V_6O_7(OCH_3)_{12}$.

	V–O _{terminal}	V–O _{bridging}	V–O _{central}
V_1	1.586	1.904, 1.920, 1.922, 1.926	2.314
V_i ($i = 2–5$)	$\langle 1.596 \rangle$	$\langle 1.982, 1.988, 2.013, 2.017 \rangle$	$\langle 2.304 \rangle$
V_6	1.5811	1.908, 1.919, 1.927, 1.930	2.217

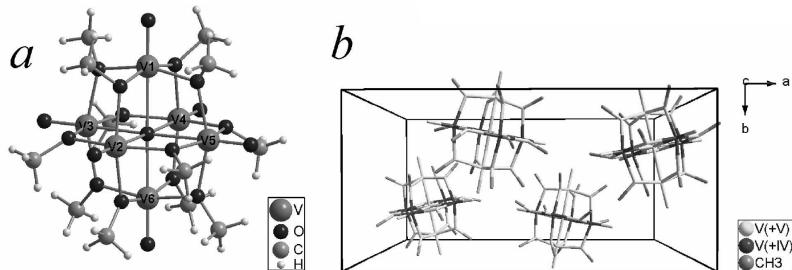


Fig. 1. (a) The structure of $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ cluster molecule; (b) the arrangement of the hexavanadium cluster in the unit cell of the $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ crystal.

vanadium nuclei all equally bind one terminal oxygen atom and four μ_2 -bridging methoxy ligands, respectively (see Table and Fig. 1 [11]). Displacement of the central oxygen toward the V_6 ion takes place. V_5 —O_{centr}— V_6 axes of the cluster-molecules deviate from [010] direction (*b*-axis of the unit cell) by 12°. The chemical contacts between cluster-molecules can be ignored.

EPR spectra of the single crystals were measured in 300–4.2 K range on an X-band RADIOPAN spectrometer with OXFORD temperature equipment. EPR has been observed in the whole temperature range. It consists of the predominant single line of Lorentzian shape and four additional signals in the magnetic field range ≈ 100 –400 mT (Fig. 2). At $T = 291$ K these signals are observed at ≈ 240 mT, 290 mT, (350 mT), and 410 mT (the third signal of this spectrum is expected in magnetic field $B \approx 340$ –350 mT, but it is overlapped with the adjacent strong signal). The parameters of various signals of these two spectra change with

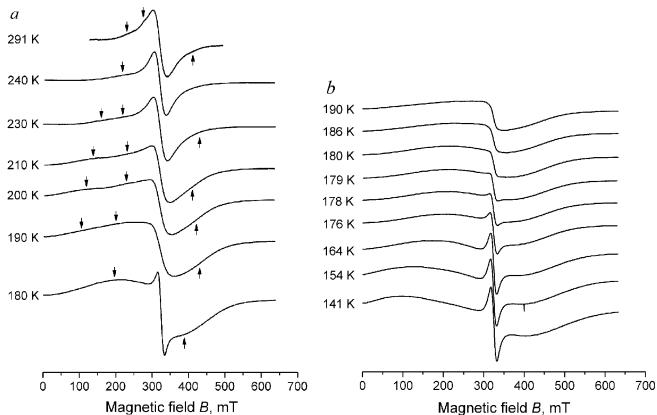


Fig. 2. Temperature evolution of the EPR spectrum (in the temperature range 291–180 K (a) and 190–140 K (b)) recorded for magnetic field B along the [010] direction of the $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ crystal. Arrows in (a) indicate signals originating from the state with $S = 2$.

temperature in a non-monotonic way. Uncorrelated changes of signals of this type continue also in lower temperatures (see below).

Figure 3 shows the temperature dependence of ΔB of the main single line spectrum. On cooling the line width decreases down to 240 K and then begins to increase reaching maximum at about 190 K. Below this temperature a rapid decrease in ΔB of the single line spectrum is observed. Temperature of this rapid change varies for various measured crystals and depends probably on the cooling rate. On further cooling the temperature dependence of the EPR signal line width is very weak and ΔB becomes 14.5 mT at 141 K, and then does not change noticeably down to 17 K, at which it increases up to 23 mT at 4.2 K. On heating a significant hysteresis is observed in the $\Delta B(T)$ dependence and ΔB does not reach the initial room temperature value. An inspection of the sample shows that it is not a single crystal one, but becomes split to small pieces.

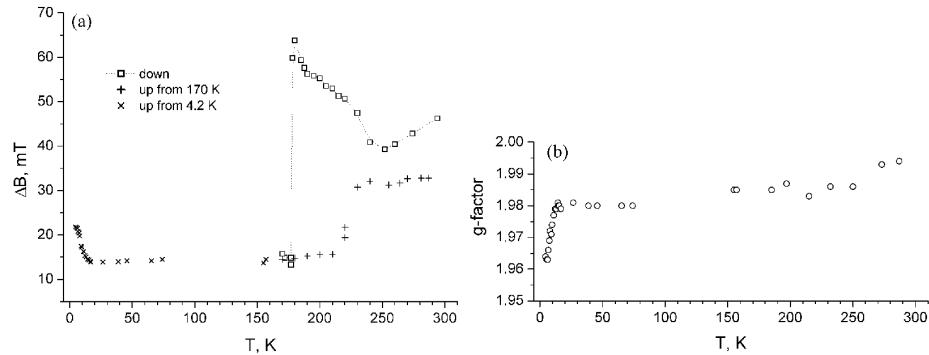


Fig. 3. Temperature dependences of the width ΔB (a) and g -factor (b) of the EPR line registered for $B \parallel [010]$ (4.2–300 K range).

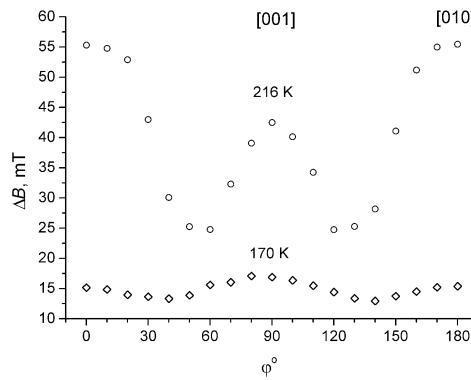


Fig. 4. Comparison of the angular dependences of the EPR line width ΔB of the predominant signal recorded in the bc plane at 216 K and 170 K.

Differences in sample properties above and below the rapid narrowing of the single line are illustrated in Fig. 4 showing the angular dependences of ΔB at 216 and 170 K. At 216 K the largest $\Delta B(\vartheta)$ is observed for $B \parallel [010]$ axis, then it reaches a minimum value at $\vartheta = 54^\circ$ and increases again up to a certain intermediate value at $\vartheta = 90^\circ$. A different picture is at 170 K. The positions of maximum and intermediate $\Delta B(\vartheta)$ values interchange, though the minimum ΔB value is again distanced from the greatest ΔB value by the angle of about 54° .

The above-described peculiarities in the $\Delta B(T)$ and in $\Delta B(\vartheta)$ for various temperatures indicate a first order phase transition, which takes place at about 180 K (depending on the cooling rate).

Changes in the g -factor of the single line are inconsiderable. Its accurate measurement is obstructed by a superposition with the signals of the additional spectrum; nevertheless, the occurrence of some regular angular and temperature dependences of g -factor is unquestionable. A sharp decrease in g -factor from 1.982 to 1.963 takes place with temperature decreasing from 18 K down to 4.2 K (Fig. 3).

These changes in the single EPR line are accompanied by changes in the four-component spectrum observed from room temperature down to 190 K. The changes are mainly distortions of the low-field and high-field wings of the single line (Fig. 2a). The change in the four-component spectrum begins at $T \approx 240$ K. An increase in ΔB and intensity of the predominant single line result in smearing of the signal at 280 mT, however, the two low-field signals are shifted to lower magnetic field, with a simultaneous increase in the interval between them, with temperature decreasing to about 190 K (Fig. 2a). The simultaneous shift of the fourth signal to the high magnetic fields is also noted. It is possible to distinguish, at $T = 200$ K, individual signals in $B \approx 100, 235$, and 400 mT. These signals are replaced at 190–180 K by a very broad signal with a still distinguishable

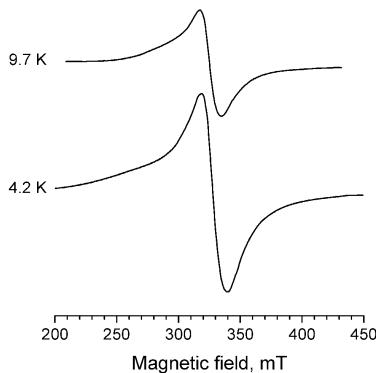


Fig. 5. EPR spectra recorded at 9.7 K and 4.2 K for magnetic field $B \parallel [010]$. Traces of the four-component spectrum related to the spin multiplets with $S = 2$ are noticeable in the low-field wing of the predominant signal.

structure. Figures 2b and 3 allow concluding about further transformation of these signals: already at 180 K a new broad signal appears. Its intensity increases and its width decreases to ≈ 180 mT at 180 K, and then it increases again ($\Delta B \approx 210$ mT at 168 K) and transforms into an extensive spectrum at $T \approx 140$ K (its extension is about 300 mT). The intensity of this spectrum quickly diminishes with temperature below 130 K, however its traces are recorded in the low-field wing of the predominant signal even at 4.2–10 K (Fig. 5).

3. Discussion

An individual V^{IV} ion has the $3d^1$ electron configuration and spin $S = 1/2$; its ground term is 2D . The nuclear spin of vanadium is $I = 7/2$, however, the hyperfine structure is not expected to be observed in the cluster including four magnetic ions due to a small value of the hyperfine splittings (A) and a relatively large width of the observed EPR line. According to the typical A values for the vanadium(IV) ion [12], the A values for clusters should be of the order of 5–0.5 mT, whereas the observed ΔB was 46–15 mT.

We shall begin the discussion of the $V_4^{IV}V_2^{V}O_7(OCH_3)_{12}$ cluster properties with the hypothetical assumption that four V^{IV} ions are localized at the V_2 – V_5 positions and linked by exchange interactions. Their $O_{\text{central}}\text{—}V\text{—}O_{\text{terminal}}$ bonds are nearly coplanar to the ac crystal plane. This supposition reflects the cluster geometrical parameters (see Table) and corresponds to the valence-sum calculations [11]. The spin Hamiltonian can thus be written as

$$\begin{aligned} H = & J_1 (S_2 S_4 + S_3 S_5) + J_0 (S_2 S_3 + S_3 S_4 + S_4 S_5 + S_5 S_2) \\ & + H_z + H_{\text{fs}} + H_{\text{hfs}}, \end{aligned} \quad (1)$$

where $S_i = 1/2$ enumerate V_i ions according to Fig. 1 and J_i are the parameters of the isotropic exchange interactions between the corresponding V^{IV} ions. H_z , H_{fs} and H_{hfs} describe the interaction of the vanadium ions with the magnetic field, the zero field splitting of the spin levels and the hyperfine interactions, respectively, which lead to the corresponding structure of the EPR spectrum. We shall choose the S_{24} and S_{35} intermediates to obtain the total spin of the cluster S . The solution of the exchange Hamiltonian is

$$\begin{aligned} E/|J_0| = & (J_1/|J_0|)[S_{24}(S_{24} + 1) + S_{35}(S_{35} + 1) - 3] \\ & + [S(S + 1) - S_{24}(S_{24} + 1) - S_{35}(S_{35} + 1)]. \end{aligned} \quad (2)$$

The spin states consist of one quintet ($S = 2$), three triplets ($S = 1$), and two singlets ($S = 0$). The signs and values of the J_i parameters determine their relative energies and it is useful to use the so-called correlation diagram for their presentation. Such a diagram (see Fig. 6) shows that in the case of the antiferromagnetic exchange (J_1 and $J_0 > 0$), assumed for the cluster in question, the lowest spin

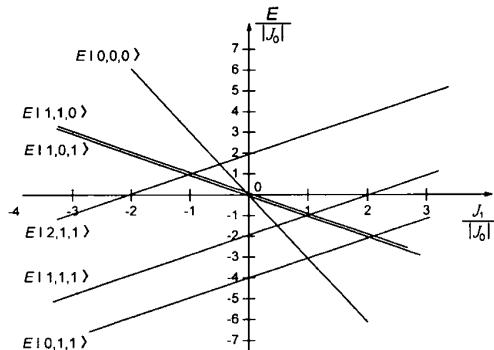


Fig. 6. The energy of the spin states of the cluster in units of $|J_0|$ as a function of $J_1/|J_0|$.

states have $S = 0$ for all values of $J_1/|J_0|$ ratio and at 4.2 K the EPR should not be observed. On the other hand, the ferromagnetic exchange would lead to a very strong temperature dependence of the spectrum, which is not consistent with the experiment.

It is seen that an isotropic exchange alone does not explain the observation of the EPR in the whole temperature interval of 300–4.2 K and the excess electron transfers between neighbouring V^{IV} and V^V sites should be taken into consideration. In the simple case of two ions in different oxidation states, the transfers of the excess electron between equivalent V^{IV}–V^V and V^V–V^{IV} states leads to the split of the spin states of the pair [13], which is characterized by the transfer parameter B . The precise solution of the problem for the hexanuclear V₄^{IV}V₂^VO₇(OCH₃)₁₂ cluster is more complicated and will be analyzed separately. Here we only suggest the tentative explanation of the observed EPR spectra behaviour in the spin Hamiltonian approach taking into account the splitting of the total spin cluster states due to the excess electron transfers.

In the starting configuration with four magnetic V^{IV} ions localized in the plane of the 6V octahedron nearly parallel to the *ac* plane of the crystal, four extra electrons can be distributed between six metallic centres in 15 ways. It means that each spin level besides the usual spin degeneracy imposed by the HDVV model has a configurational 15-fold degeneracy. The account of the electron transfer leads to the splitting of spin multiplets and also to mixing of states characterized by the same total spin. If the parameter(s) of the electron transfer is (are) of the same order as the exchange parameter, the order of spin levels can be rather complicated. In particular, as it will be demonstrated in our future publications, for a certain relationship between these parameters, the ground state can have a non-zero spin.

All these explain the fact that EPR is observed in the whole temperature interval 291–4.2 K and the fact that the predominant single signal and the additional spectrum are observed simultaneously in the entire temperature range.

In our case EPR is observed on the total spin states with $S = 1$ and 2. We relate the observed four signal spectrum to transitions within the spin multiplets with $S = 2$. This means that the residual predominant signal should originate from $S = 1$ states. An absence of the fine structure and the Lorentzian shape of this signal suggest the presence of a process quick enough to average the anisotropic exchange and dipole-dipole interactions — the reasons for fine structure of the EPR spectrum. At 291 K and for the magnetic field $\mathbf{B} \parallel [010]$ direction, the intervals between EPR signals in the spectrum corresponding to the $S = 2$ state can be estimated as about 50 mT. The whole extension of the EPR spectrum for the $S = 2$ state (including the extension increase due to the unresolved hyperfine structure) covers 180 mT. This allows an estimation of the fine structure parameter $D_{(\text{quint})} \approx 0.025\text{--}0.3 \text{ cm}^{-1}$. Let us accept that $D_{(\text{quint})} \approx D_{(\text{triplet})}$. The condition $\nu_{\text{tr}} \gg 2D_{(\text{triplet})}/h$ should be fulfilled for averaging the fine structure of the $S = 1$ states. One can consider that $\nu_{\text{tr}} \approx 0.6 \times 10^{10} \text{ s}^{-1}$ is sufficient for such an averaging (and not sufficient for averaging the $S = 2$ states fine structure even at $T = 291$ K). We have mentioned above that inter-cluster exchange interactions cannot influence the spectra behaviour (the uncorrelated temperature changes in the predominant EPR line and the four-component spectrum are considered as the strongest argument for this conclusion). This means that the averaging considered occurs due to some intramolecular dynamic process. We suppose that the intramolecular electron transfer is such a process.

Let us consider the observed temperature behaviour of the EPR spectrum. Its main manifestation for the T -interval 291–200 K is the broadening of the predominant single signal below 250 K and a simultaneous increase in the splitting between the signals of $S = 2$ spectrum. Taking into consideration small distinctions in all V_i –O bonds, the splitting of the spin states for different V^{IV} ion configurations due to one-jump transfers can be different. This increases the number of the spin states. But at the same time, the transitions between configurations are possible and their rate can be insufficient for a complete averaging of the spectrum. Thus, the temperature dependence of the line width of the single EPR signal would be stipulated by an increase in the weight of the corresponding spin states with decreasing temperature. However, other reasons should be also taken into account.

It is obvious that the spectrum transformation in the range of 190–150 K reflects the existence of the first order phase transition in the $V_4^{\text{IV}}V_2^{\text{V}}O_7(\text{OCH}_3)_{12}$ crystal. The temperature decrease leads to changes in the lattice and cluster geometrical parameters and thus in the cluster dynamics. The abrupt changes in the single signal ΔB (its narrowing down to 20 mT requires the increase in ν_{tr} at least up to $(2\text{--}3) \times 10^{10} \text{ s}^{-1}$) take place in a very narrow temperature interval near 180 K. However, the changes in ΔB , and especially the uncorrelated transformations of $S = 2$ spectra, occur in a much wider temperature interval $\approx 200\text{--}140$ K. The change in the character of the angular dependence of the predominant signal

line width ΔB after the phase transition indicates a change in the most probable localization of V^{IV} ions in the V₄^{IV}V₂^VO₇(OCH₃)₁₂ molecule to the positions V₂V₄V₁V₆ instead of V₂₋₅ ones.

We suppose that the gradual changes in the structural parameters start far from a sharp transition temperature and that quenching of some modes of the lattice vibrations and an increase in the frequencies of the other modes take place in the vicinity of the transition [14].

We shall also mention, as an interesting observation, the gradual broadening of the $S = 2$ spectrum accompanied by a sharp decrease in its intensity below 170 K down to 130 K. (The intensity of the $S = 1$ signal does not change noticeably down to about 20 K.) This is obviously connected with the diminishing of the $S = 2$ states population. One can estimate their energies as being in the range $\approx 90\text{--}120\text{ cm}^{-1}$. At the same time, the influence of $S = 2$ signals on the shape of $S = 1$ signal even at the temperatures 4.2–10 K shows that some of the $S = 2$ states have smaller energy.

The temperature dependence of g -factor can be explained by a few reasons. The obvious one is connected with a change in the directions of the symmetry axes of V^{IV} configurations, represented by different energy states. Another reason is connected with the spin states origin and with their dependence on the intermediate spin values. We shall analyze $g(T)$ dependence for the 4.2–17 K interval, where it is particularly strong.

Let us consider magnetic properties of the states with $S = 1$ in the framework of the spin Hamiltonian (1) [15]. These states are distinguished by values of an intermediate spin S_{24} and S_{35} (see the correlation diagram in Fig. 6). Let us direct the magnetic field \mathbf{B} along V₂–O_{central}–V₄ direction and write the expression for the Zeeman energy of the cluster in the form

$$\begin{aligned} g\beta BS &= g_{\parallel}^{\text{ind}}\beta B(S_2 + S_4) + g_{\perp}^{\text{ind}}\beta B(S_3 + S_5) = g_{\parallel}^{\text{ind}}\beta BS_{24} + g_{\perp}^{\text{ind}}\beta BS_{35} \\ &= (1/2)(g_{\parallel}^{\text{ind}} + g_{\perp}^{\text{ind}})(S_{24} + S_{35}) + (1/2)(g_{\parallel}^{\text{ind}} - g_{\perp}^{\text{ind}})(S_{24} - S_{35}), \end{aligned} \quad (3)$$

where $g_{\parallel}^{\text{ind}}$ and g_{\perp}^{ind} are the components of the g -factor of the individual V^{IV} ion. One can get the following expression for the cluster g -factor

$$g = (1/2)(g_{\parallel}^{\text{ind}} + g_{\perp}^{\text{ind}}) + (g_{\parallel}^{\text{ind}} - g_{\perp}^{\text{ind}})\frac{S_{24}(S_{24} + 1) - S_{35}(S_{35} + 1)}{2S(S + 1)}. \quad (4)$$

This means that for $g_{\parallel}^{\text{ind}} < g_{\perp}^{\text{ind}}$ the cluster g -factor for the state $E|1, 1, 1\rangle$ should differ from g -factors for the states $E|1, 0, 1\rangle$ and $E|1, 1, 0\rangle$ by a value of $|(g_{\parallel}^{\text{ind}} - g_{\perp}^{\text{ind}})/2|$. Even very small distortion of the cluster removes the degeneracy of the $E|1, 0, 1\rangle$ and $E|1, 1, 0\rangle$ states. Therefore, we shall accept the following order of the lowest energy levels: $E|1, 1, 0\rangle$ is lower than $E|1, 1, 1\rangle$ lower than $E|1, 0, 1\rangle$ or $E|1, 1, 0\rangle$ is lower than $E|1, 0, 1\rangle$ lower than $E|1, 1, 1\rangle$.

In our approach, the observed g -values of the V₄^{IV}V₂^VO₇(OCH₃)₁₂ cluster represent the averaged values of the basic 4V^{IV} configuration and configurations

formed after the electron transfers. Let us show that the conclusion on g -factors dependence on intermediate spin is still valid if we consider just a transfer of single electron to the neighbouring metal centre. Let us write the exchange Hamiltonian for one of $4V^{IV}$ configurations resulting after one-jump transfer

$$H = J_{24}S_2S_4 + J_1(S_2S_3 + S_3S_4) + J_0(S_1S_2 + S_1S_3 + S_1S_4) \quad (5)$$

and the expression obtained after its solution for the energies of the spin states

$$\begin{aligned} E = J_{24}[S_{24}(S_{24} + 1) - 2S_2(S_2 + 1)] - J_1[S_{234}(S_{234} + 1) - S_{23}(S_{23} + 1)] \\ - S_2(S_2 + 1)] + J_0[S(S + 1) - S_{234}(S_{234} + 1) - S_1(S_1 + 1)]. \end{aligned} \quad (6)$$

The magnetic properties of the states of $S = 1$ are distinguished now by the values of an intermediate spin S_{234} . The expression for the cluster g -factor now is as follows:

$$g = (1/2)(g_1^{\text{ind}} + g_2^{\text{ind}}) + (g_2^{\text{ind}} - g_1^{\text{ind}}) \frac{S_{234}(S_{234} + 1) - S_1(S_1 + 1)}{2S(S + 1)}. \quad (7)$$

The cluster g -factor depends now on the value of an intermediate spin S_{234} . For example, if $g_1^{\text{ind}} > g_2^{\text{ind}}$, the g -factor for the state $E|1, 3/2, 1\rangle$ should be smaller than for the state $E|1, 1/2, 1\rangle$ and the energy state $E|1, 3/2, 1\rangle$ has the smallest energy in the $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ cluster. We see that above obtained conclusions of the g -factor dependence on an intermediate spin and the determination of the low energy state have been confirmed.

4. Conclusions

Our results have shown that the temperature behaviour of the mixed-valence $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ cluster EPR spectra cannot be explained within a purely static HDVV model. We propose an explanation of the observed peculiarities by introducing the internal dynamics due to intramolecular electron transfers. In principle, such electron jumps must completely modify the energy spectrum. Our preliminary simplified analysis suggests that, probably, the electronic delocalization within the cluster should be characterized not by a single, but by several electron transfer parameters. Also, different configurations connected through the electron transfer can have different energy. The conclusions about the arrangement and relative energies of the total spin states, obtained assuming a single electron transfer, are believed to reflect the physical content of the problem in question and should be considered as a departure point for a more adequate theoretical analysis. We consider our explanation as a possible one, however, the existence of dynamic processes in the studied $V_4^{IV}V_2^V O_7(OCH_3)_{12}$ should be considered as the experimental fact.

At last, we should emphasize a very interesting peculiar feature of the crystal studied explained by the occurrence of a phase transition and the following

breakdown of the crystal mechanical properties. This feature will be a subject of further work.

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