The EPR evidence of local hydrogen bond distortion evoked by VO^{2+} ions in $K_3H(SO_4)_2$ crystals

LETTER TO THE EDITOR

The EPR evidence of local hydrogen bond distortion evoked by VO^{2+} ions in K$_3$H(SO$_4$)$_2$ crystals

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Abstract. An investigation of the influence of the proton subsystem on the EPR spectra of VO^{2+} ions in K$_3$H(SO$_4$)$_2$ is performed. The EPR superhyperfine structure from protons and their temperature dependences manifest the existence of asymmetrical configurations of protons at low temperatures. The preserving of the double-minimum character of proton potential on bonds in the near vicinity of VO^{2+} ions is realized. It is suggested to be caused by redistribution of electron charges.

Tripotassium hydrogen disulphate K$_3$H(SO$_4$)$_2$ has a unique character from the viewpoint of the phase transition among hydrogen bonded materials. First of all, the deuterium compound K$_3$D(SO$_4$)$_2$ has a finite phase transition temperature ($T_c = 85$ K) while the hydrogen compound does not show any phase transition [1, 2]. Recent structure analysis of K$_3$H(SO$_4$)$_2$ and K$_3$D(SO$_4$)$_2$ revealed that the structures are isomorphous with each other, and the difference of positional parameters is extremely small [3, 4]. That is why the tunnelling model [5] and concepts usually called the 'geometrical isotope effect' [6] are used to explain the isotope effect.

We have studied the EPR spectra of K$_3$H(SO$_4$)$_2$ doped with VO^{2+} ions, grown by the isothermal method described elsewhere [7]. Because the VO^{2+} records the superhyperfine EPR spectra from protons, it should be a sensitive probe of proton motion versus temperature.

In accord with our data the main VO^{2+} hyperfine structure spectra (their spin-Hamiltonian parameters and direction cosines of electric field gradient) are only slightly different from those in (NH$_4$)$_3$H(SO$_4$)$_2$ [7, 8], but the presence of superhyperfine structure with two *close* protons allows us to place unambiguously the VO^{2+} ion into the K$^+$ site position.

The EPR spectrum of VO^{2+} with resolved superhyperfine structure is shown in figure 1. This superhyperfine structure consists of three lines with intensity ratio 1:2:1 at RT and it is smeared out at about 380 K due to the onset of proton conductivity. Nevertheless this spectrum is fully reversible after the next temperature lowering. The superhyperfine structure line positions versus temperature are shown in figure 2, where it is clearly evident that at about 235 K this triplet spectrum slowly transforms to the quartet characteristic for one *close* and one *far* (distant) proton near the oxygen formed square pyramid of the VO^{2+} complex.
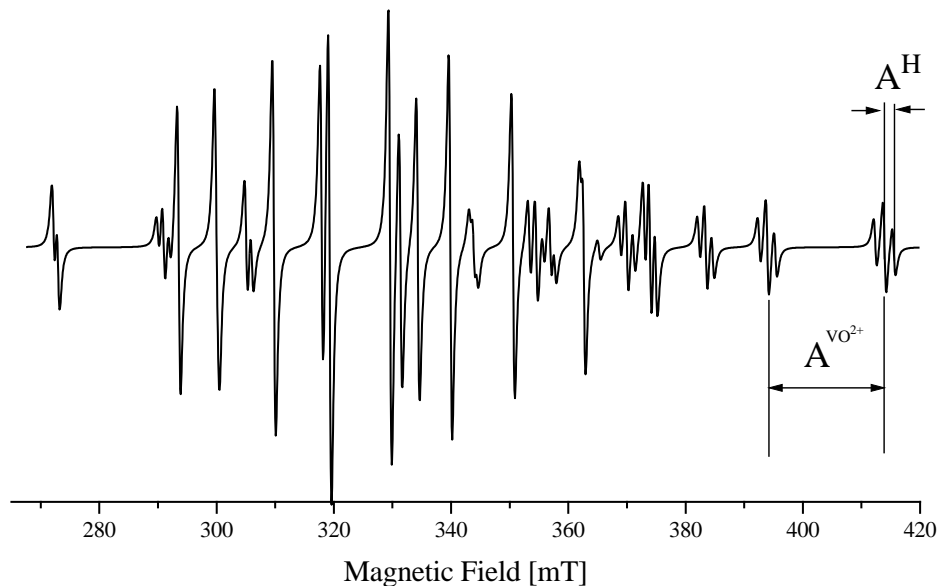
Figure 1. The EPR spectrum of VO^{2+} in $K_3H(SO_4)_2$ with hyperfine and superhyperfine structure.

The temperature dependences of the nature of the hydrogen bond both in $K_3H(SO_4)_2$ and $K_3D(SO_4)_2$ were investigated in x-ray experiments by Noda *et al* [3, 4], who measured the hydrogen bond length $R_{OO}(H) = 2.493$ Å and $R_{OO}(D) = 2.518$ Å at room temperature. The critical bond length is estimated [4] as $r_c(H) = 2.47$ Å and $r_c(D) = 2.44$ Å. According to the structural data, the protons take a two site state when the hydrogen bond length R_{OO} is longer than the critical bond length r_c. The crossover of $R_{OO}(H)$ and r_c was suggested [9] at about 100 K and the conclusion was drawn that the double feature of hydrogen atoms changes into a single state at the centre of the hydrogen bond. Our EPR data are inconsistent with the 'geometrical model' presented above.

We may conclude from the above mentioned experimental data that nearest hydrogen bonds in the vicinity of VO^{2+} ions remain with double wells at low temperatures. The local influence of VO^{2+} ions may be explained on the basis of the assumption that the additional positive charge of the impurity may be compensated not only by the presence of the nearby located proton vacancy but also by electron charge redistribution, in particular by increase of electron density on orbitals localized on neighbour oxygen ions. This may cause the change of proton adiabatic potential on the bond. As obtained by means of quantum chemical calculations [10], the increase of mean number n of electrons on the hydrogen bond results in a decrease of the critical value R_{OO} of bond length at which the two potential minima join into a central one ($\Delta R = -0.04$ Å at $\Delta n = 0.2$). Data given in [11] (where the role of hydrogen bonds for electron properties of transition-metal compounds was investigated) also point out the correlation between the excess electron charge on one end of the hydrogen bond and the possible proton localization.

The situation when the double-well character of hydrogen bonds remains in the near vicinity of VO^{2+} ions is similar to that found in the case of Tl^{2+} impurities in KH_2PO_4 [12]. The presence of the Tl^{2+} in KH_2PO_4 with its extra charge causes one near-neighbour proton in the H_2PO_4 configuration to be a distant site instead of a close one leading to the inversion
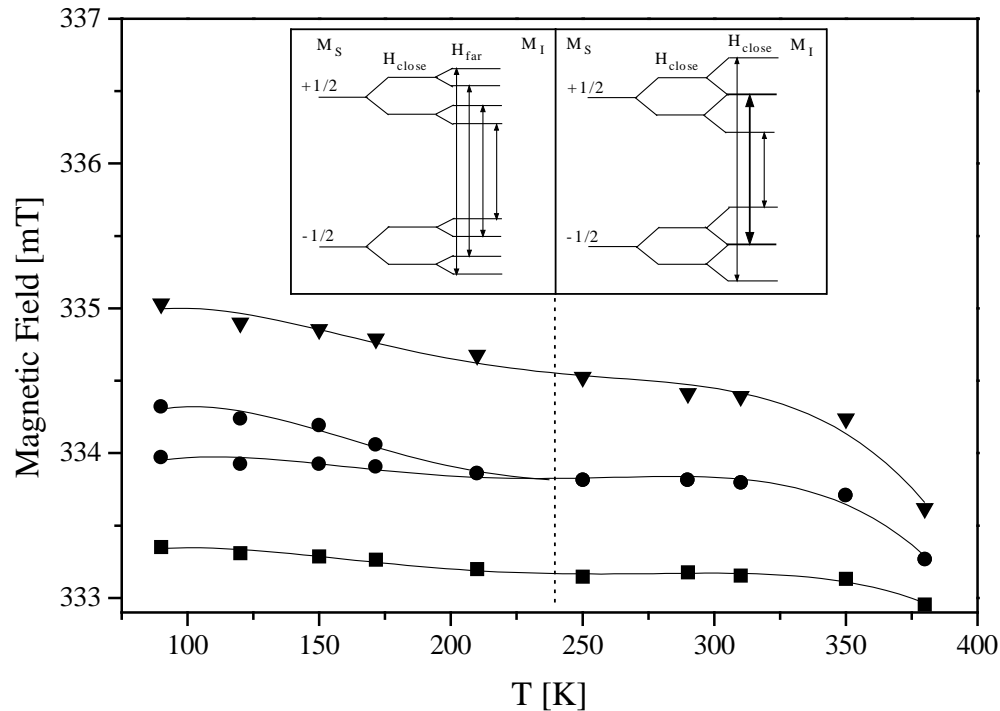
Figure 2. The superhyperfine structure (from protons) of VO^{2+} line positions in $K_3H(SO_4)_2$ versus temperature. In abbreviation the scheme of VO^{2+} $\pm 7/2 \leftrightarrow \pm 7/2$ hyperfine line splitting due to the presence of two equivalent and two nonequivalent protons is shown.

of the Slater configuration in one of the H_nPO_4 groups. On lowering of temperature instead of the uniform distribution of protons on nearest bonds the asymmetrical configuration is realized: on one bond the proton is in the nearest well and on the other in the distant well. Such a configuration looks energetically preferable giving an additional compensation of impurity excess charge.

We have to point out that in $K_3H(SO_4)$ crystals with a dimer-like structure of the hydrogen bond network with a symmetrical one-well potential at low temperature the incorporation of an ion with an additional excess charge (like VO^{2+}) leads to the local distortion of the potential well bonds. The local double-well potential is preserved and asymmetrical proton configurations are energetically favourable. Then in the EPR experiment the superhyperfine structure due to two nonequivalent protons i.e. *close* with $A_{close} = 9.7$ G and *far* (distant) $A_{far} = 3.7$ G can be understood.

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