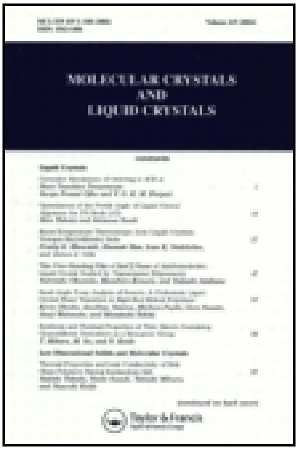

Molecular Crystals and Liquid Crystals

Magnetic Resonance Studies of Quasi-One-Dimensional Conductor β-$M_xV_2O_5$

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MAGNETIC RESONANCE STUDIES OF QUASI-ONE-DIMENSIONAL CONDUCTOR β-$M_xV_2O_5$

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In quasi-one-dimensional conductor β-$Na_{.33}V_2O_5$, the commensurate C.D.W.(dimerization) phase transition about 180 K was found by the magnetic resonance and X ray diffuse scattering studies. The pair formation of magnetic V^{4+} ions in site I chain has been discussed on the basis of the spin-lattice relaxation time of ^{23}Na and ^{51}V nuclei and the anisotropic EPR line width.
In case of β-$Li_xV_2O_5$ (x=0.36), the interesting two phase transitions were observed, 1) the incommensurate C.D.W. phase appears about 220 K, 2) below 170 K, this C.D.W. phase (q_b=0.53) splits two sublattice of the commensurate C.D.W. phase (q_b=0.5) and the I.C.C.D.W. phase (q_b=0.57). The magnetic resonance studies of the single crystals of β-$Li_xV_2O_5$ show that there occur the microscopic changes of the electronic structure corresponding to these phase transitions.

It has recently been revealed in electric conductivity measurements(1) on a single crystal of β-$Na_{.33}V_2O_5$ that this material is one of new quasi-one-dimensional conductor. The observed value of conductivity along the b axis is $100\Omega^{-1}cm^{-1}$ at 300 K and two order of magnitude larger than that perpendicular to the b axis, and its temperature dependence is semi-conductor-like.

According to the structural data(2), the vanadium atoms are situated at the center of the deformed octahedron of oxygen atoms and these make complex ladder extending along the monoclinic b axis which is the most conductive axis. There are three inequivalent crystallographic sites of vanadium atoms. The alkaline metal ions are accommodated in tunnels of oxygen atoms running parallel to the b axis. It has been observed in NMR measurements(3,4) that ^{23}Na, and ^{7}Li nuclei have not any Knight shift; consequently the sodium and lithium ions are monovalent and have donated their outer s-shell electrons to the vanadium ions.

There naturally arise the questions, in which vanadium sites these donated electrons occupy? and what is the conduction mechanism of the anisotropic conductivity of these materials?

In [1] we discuss the problem of β-Na$_{,33}$V$_2$O$_5$, in which the V^{4+}ions were found to occupy the half of the vanadium position of site I and this fact implys the commensurate condition may realize. The dynamics of the electron hopping motion are discussed on the basis of the magnetic resonance results. In [2], we discussed the problem of the β-Li$_x$V$_2$O$_5$($0.22 \lesssim x \lesssim 0,37$), where the donar concentration is variable by proper doping of Li ions within the limit as shown above. Therefore, the Incommensurate C.D.W. is expected in this system. The X ray difuse scattering results showed the existence of the I.C.C.D.W. state.

The X ray diffuse scattering studies have been carried out on β-Li$_{,36}$V$_2$O$_5$. The two C.D.W. phases were observed in following temperature regions.

(I) 180 K < T < 220 K

In this temperature region, Incommensurate C.D.W. state of wave number q=(0, 0,53, 0) developes gradually. The coherence length of this C.D.W. state is estimated to be longer than several tens atomic distance, though present results are limitted by the instrumental resolution.

(II) T < 170 K

The above mentioned I.C.C.D.W. state (q_b=0.53) splits to two sublattices of Commensurate C.D.W. state of q=(0, 0.50, 0,50) and Incommensurate C.D.W. state of q=(0, 0.57, 0.12~0.13). These results show that the C.C.D.W. chains put in order every two unit cells perpendicular to the chain axis. Another I.C.C.D.W. chains have the long range arrangement of ~ 8 times of unit cells(120 A).

In order to study the details of these phase transitions and the coexistence of two kinds of C.D.W. state, we have carried out the measurements of electron paramagnetic resonance and N.M.R. studies of ^{7}Li and ^{51}V nuclei in this system. The experimental results related with these phase transitions are discussed from microscopic view point of the transition of the electronic states of vanadium atoms.

[1] β-$Na_{.33}V_2O_5$ (Commensurate case)

Recently we carried out the precise measurements of anisotropy of g-value of EPR absorption signal in β-$Na_{.33}V_2O_5$(5).

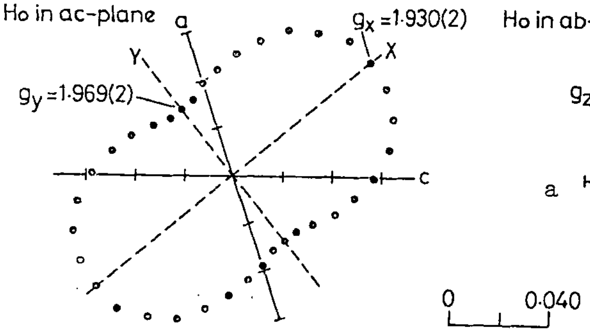


Fig.1. A polar diagram of the angular dependence of g-shift from free electron value at 77 K.

The principal axes X, and Y lie in the monoclinic ac plane and Z axis coincide with the b axis. Refering with the structural data(2), one can see that the principal axes X, Y, and Z coincide with those of the distorted octahedron of oxygen surrounding of the site I position of vanadium. This fact indicates that the magnetic V^{4+} ions primarily occupy the site I positions (Fig.2 a).

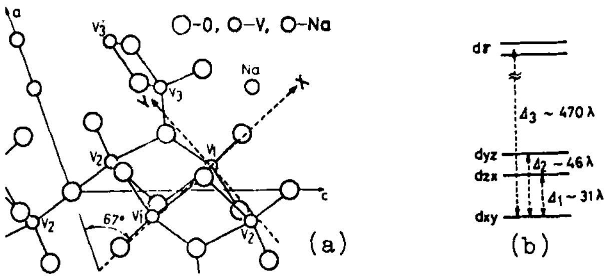
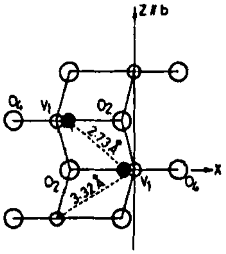
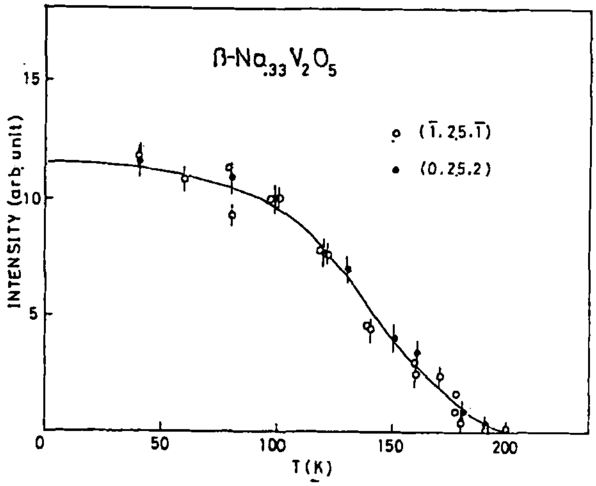


Fig.2 a. Crystal structure in the vicinity of V(I) site projected onto an ac-plane and principal axes of g-tensor.
Fig.2 b. Energy level configuration of $(3d)^1$ electron.

The ground state of $(3d)^1$ electron in V^{4+} ions is d_{xy} state. However, if we consider the relative position of the vanadium ions in site I to the oxygen octahedron, d_{xy} state does not seem to be favorable for the ground state, because one of the neighbouring oxygen has the shortest distance from V ions in site I (F.g.2 a). In order that the level configuration derived above is realized, V^{4+} ions must have shifted from the original position towards the center of the oxygen octahedron. This displacement reduces the relative distance between V^{4+} ions in the zigzag chain of siteI, we suppose that the displacement is caused by a dimerization of V^{4+} ions as shown in Fig.3 a. Recent X ray diffuse scattering results show the existence of the dimerization along b axis(Fig.3 b).



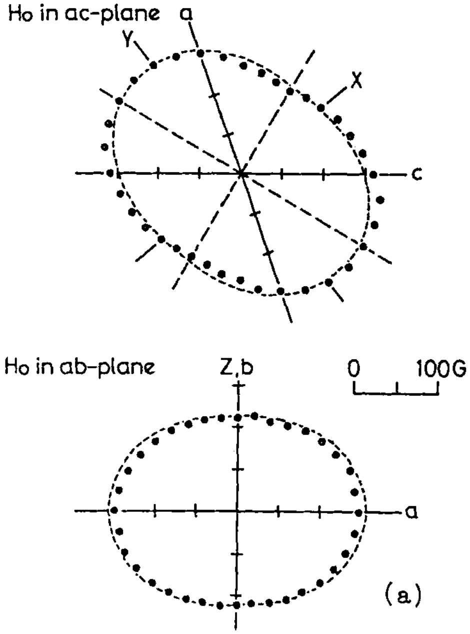
a



b

Fig.3 a. Displacement of V(I) position proposed in text.
Fig.3 b. Temperature dependence of the intensity of X ray diffuse scattering peaks.

The angular dependence of the peak to peak line width of the absorption derivative at 77 K is shown in Fig.4 as a polar diagram. The most probable mechanism of anisotropic line width is dipolar coupling between the magnetic ions. The dipolar field μ_B/r^3 is estimated as 460 G. using the pair distance of 2.73 A after displacement. Since the observed line shape is pure Lorentzian, the dipolar field is expected to be narrowed by the relative motion of electron. The line width, that is, the transverse relaxation rate by this mechanism is calculated by using the spectral density



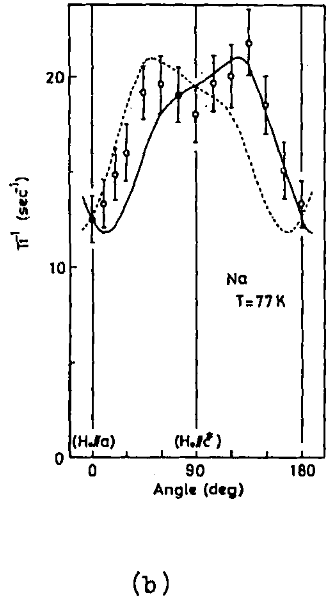


Fig.4 a. A polar diagram of the angular dependence of the the linewidth at 77 K. Broken curves are theoretical ones calculated on the basis of the pairing model. (5)
Fig.4 b Angular dependence of spin-lattice relaxation rate of ^{23}Na nuclei in ac-plane at 77 K, and solid and dotted lines are calculated ones. (6)

of the fluctuating dipolar field;

$$1/T_2 = (g\mu_B)^4\hbar^{-2}S(S+1)\,_{k\neq j}\left[\frac{3}{8}J^{(2)}_{jk}(2\omega_z) + \frac{15}{4}J^{(1)}_{jk}(\omega_z) + \frac{3}{8}J^{(0)}_{jk}(0)\right],$$

where g, μ_B, S and ω_z are g-value, Bohr magneton, spin and electron Zeeman frequency, respectively. The spectral density $J^{(q)}(\ )$ are the Fourier transform of the correlation function $G^{(q)}(\tau)$ given as

$$G^{(q)}(\tau) = \overline{F^{(q)}(t)F^{(q)*}(t+\tau)}$$

by using the geometrical factors of dipolar coupling $F^{(0)} = r^{-3}(1-3\cos^2\theta)$, $F^{(1)} = r^{-3}\sin\theta\cos\theta e^{-i\phi}$, and $F^{(2)} = r^{-3}\sin^2\theta e^{-2i\phi}$ where (r, θ, ϕ) are the polar coordinate of of the vector connecting a certain pair of electrons with respect to the field direction. The qualitative agreement was obtained only when we consider a pair correlation along site I chain, The calculation of the contribution from intra-pair dipolar interaction was modified as follow: The existence of hopping motion of pairs along the zig-zag chain accompanied by a rapid alternation of pair direction, much higher than the Zeeman frequency ω_z, was assumed. The decay of the average correlation function is characterized by a time $\tau_{dep.}$ at which the pair correlation is destroyed. Using $\tau_{dep.}$ and τ_c as fitting parameter, we have obtained the best fit with the observed angular dependence as shown in Fig.4 a. The main relaxation rate comes from the intra-pair interaction and the depairing time $\tau_{dep.}$ was determined as 1.6^{-11} sec.. The correlation time ,charaterized as the interpair effect, was found about one half of $\tau_{dep.}$.

The rapid hopping motion of the magnetic electrons causes the fluctuating dipolar magnetic field at ^{23}Na nuclei and contributes the spin-lattice relaxation mechanism. The angular dependence in ac-plane of spin-lattice relaxation rate of ^{23}Na nuclei is shown in Fig.4 b. The relaxation rate due to the magnetic dipolar interaction is given by:

$$1/T_1 = \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1)[\frac{1}{12} J^{(0)}(\omega_I-\omega_S) + \frac{3}{2} J^{(1)}(\omega_I) + \frac{3}{4} J^{(2)}(\omega_I+\omega_S)]$$

where γ_I,and γ_S, ω_I,and ω_S, and S are gyromagnetic ratios of necleus and electron, nualear and electron Zeeman frequencies, and spin number, respectively. $J^{(q)}$ is spectral density as given before. On the basis of cw-NMR results(3), there are two vanadium sites such as site I and III, which have possibility to be magnetic. Thus, the spin-lattice relaxation of ^{23}Na nuclei can be considered by two components, *from* V^{4+} ions in site I and III,

$$1/T_1 = 1/T_1(I) + 1/T_1(III).$$

The best fitting was obtained when parameters are chosen as $p_1\tau_1 \sim 7.7\text{x}10^{-13}$ sec.,$p_3\tau_3 \sim 6.7\text{x}10^{-13}$ sec.,and the calculated results were shown in Fig.4 b as solid and dotted lines, where p_1,p_3 mean the occupation probabilities of electrons at site I and III respectively, $p_1 + p_3 = 0.5$ was required by sodium content, EPR results indicate $p_1 \sim 0.5$. τ_1,τ_3 are the correlation time of electron hopping motion at each site.

In conclusion, present magnetic resonance studies show that the electron pairing state exists in β-$Na_{.33}V_2O_5$ and it moves in site I zig-zag chain along b-axis, which indicates that this new type of electron hopping motion seems to be the origin of quasi-one-dimensional conductivity of this material.

[2] β-$Li_xV_2O_5$ (Incommensurate case)

In β-$Li_xV_2O_5$ system, the detailed phase diagram(7) shows that β phase exists in the region of Li concentration, $0.22 \leq x \leq 0.37$. We found that the microscopic physical properties measured by NMR and EPR show the characteristic behavior only in the narrow concentration of Li dopant between $0.28 \leq x \leq 0.37$. General behaviors are rather similar to those in β-$Na_{.33}V_2O_5$, though there are lot of differences in details. The Li samples, out-side of this concentration region, show that the vanadium ions seems to be almost non magnetic penta-valent state, as far as the experimental results of NMR and EPR are concerned.

The temperature dependence of the intensity of X ray diffuse scattering peaks are shown in Fig.5. There exist two interesting phase transitions, one is around 220 K and another is around 170 K.

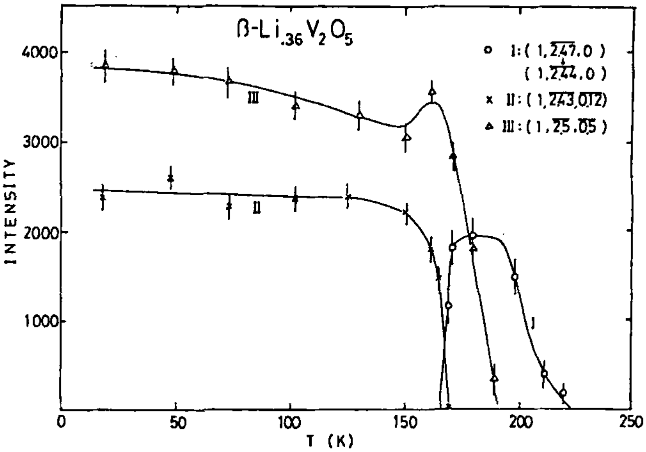
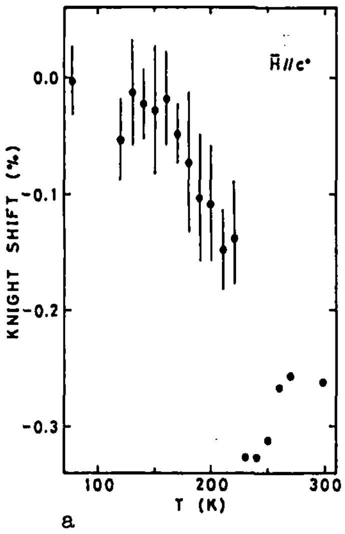


Fig.5 The temperature dependence of the intensity of X ray diffuse scattering peaks of β-$Li_{.36}V_2O_5$.

In the temperature range 180 K< T< 220 K, the Incommensurate C.D.W. state of wave number $q_{I.C.} = (0,0.53,0)$ developes gradually. On the other hand, below 190 K the another C.D.W. state of $q_C = (0\ .\ ,0.5,0.5)$ grows up. It should be noted that the wave number of I.C.C.D.W. $q_{I.C.}$ decreases monotonously corresponding to the growth of the commensurate C.D.W. state. At the temperature below 170 K, the above mentioned IC.C.D.W. state splits to two sublattices of C.C.D.W. state of $q=(0,0.50,0.50)$ and IC.C.D.W. state of $q=(0,0.57,0.12\sim0.13)$. These results indicates that the C.C.D.W. chains have an ordering of two times of unit cells parallel to the c axis. Another IC.C.D.W. chains have the long range spatial period of ~8 times of c lattice parameter(~120 A).



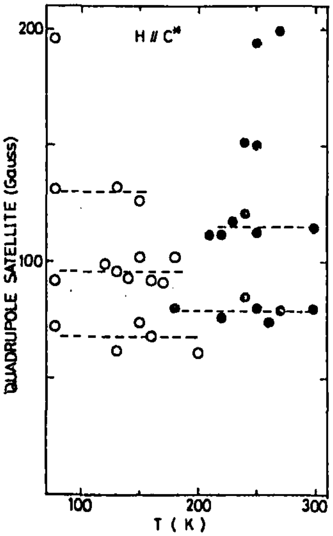


Fig.6 a Temperature dependence of the Knight shift of ^{51}V nuclei in β-Li$_{.36}$V$_2$O$_5$.

Fig.6 b Temperature dependence of quadrupole satellite of ^{51}V nuclei in β-Li$_{.36}$V$_2$O$_5$.

From the experimental results of NMR as shown in Fig.6a ,b, one can expect that β-Li$_{.36}$V$_2$O$_5$ undergoes the first order phase transition around 220 K, and there occurs the big change of the electronic states of vanadium ions in this material.

REFERENCES

1. R.H. Wallis, N. Sol and A. Zylbersztejn, Solid State Comm. 23 539 (1977).
2. H. Kobayashi, Bull.Chem.Soc.Japan 52 1315 (1979).
3. K. Maruyama and H. Nagasawa, J.Phys.Soc.Japan 48 2159 (1980).
4. J. Gendell, R.M. Cotts and M.J. Sienko, J.Chem. Phys. 37 220 (1962).
5. T. Takahashi and H. Nagasawa, Solid State Comm. to be published.
6. T. Erata, T. Takahashi and H. Nagasawa, Solid State Comm. 39 (1981).
7. J. Galy et al., J.Solid State Chem. 1 339 (1970).