

NMR AND EPR STUDIES ON QUASI-ONE-DIMENSIONAL
CONDUCTOR $\beta\text{-M}_x\text{V}_2\text{O}_5$

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The existence of valence fluctuation between V^{5+} and V^{4+} states and a first-order structural transition around 150K were confirmed by NMR of ^{51}V nuclei. The correlation time of the electron hopping is estimated as 4×10^{-11} sec at 300K from the observed spin-lattice relaxation time of ^{23}Na . Displacement of V_1 position as this site is occupied by V^{4+} ions is proposed by an analysis of the anisotropic g-value.

Recently, $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ has been revealed to be a highly anisotropic conductor, whose conductivity along the monoclinic b-axis is about $100 \Omega^{-1}\text{cm}^{-1}$ and two order of magnitude larger than that perpendicular to the b-axis [1]. In order to make clear the conduction mechanism from microscopic point of view, magnetic resonance and relaxation measurements on single crystal of this material were carried out, in the temperature range between 90K and 300K.

The cw-NMR measurement of ^{23}Na nuclei shows that the resonance line have nearly zero Knight shift, which indicates that the sodium ions in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ are monovalent. Two central resonance lines of ^{51}V nuclei were observed in the magnetic field parallel to the b-axis (Fig.(1)); the one has a small positive Knight shift and a narrower linewidth, and another broader line has a negative Knight shift originating from 3d-electrons. The relative signal intensity of the former is one-half of the latter. We can attribute the former to non-magnetic V^{5+} ions at one of the three sites of V, probably site II [2], and the latter to mixed valence states of V^{5+} and V^{4+} , with electron hopping between the other two sites (site I and III). This result is one of microscopic evidences for the existence of valence fluctuation, which can be considered as the origin of the anisotropic conductivity of this material. The correlation time τ_c of the electron hopping can be estimated from the observed spin-lattice relaxation time T_1 of ^{23}Na nuclei (Fig.(3)), assuming dipolar relaxation due to the magnetic V^{4+} ions. Neglecting the angular dependence, we obtain $\tau_c \sim 4 \times 10^{-11}$ sec at 300K.

The temperature dependence of ^{51}V satellite position clarifies the occurrence of a first-order structural transition in the temperature range between 130K and 170K (Fig.(2)). This structural transition, however, does not cause serious change in the electronic properties such as spin-susceptibility and NMR- and EPR- relaxation. There has been no significant difference of X-ray diffraction pattern in a powder sample at 77K and the room temperature [3]. These results suggest that the observed structural transition originate from only small displacement of a part of constituent atoms. The measured

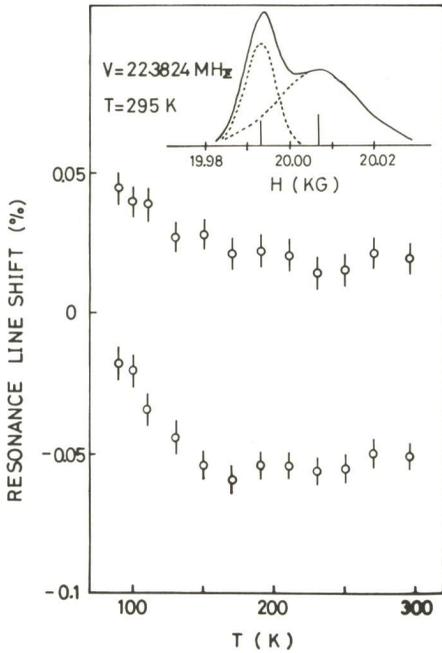


Fig. 1 Temperature dependence of ^{51}V resonance line shift and absorption line shape at 295K

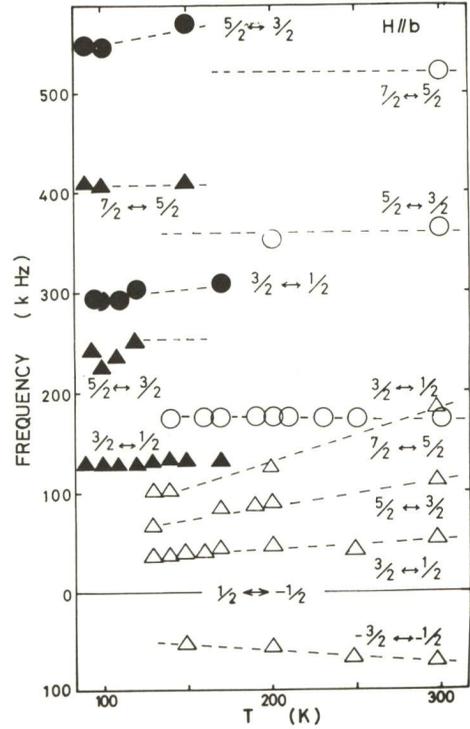


Fig. 2 Temperature dependence of ^{51}V nuclear quadrupole satellites (O---site I & III, Δ ---site II)

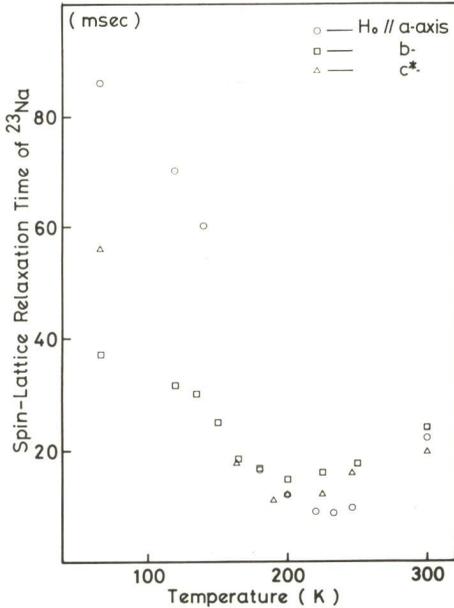


Fig. 3 Temperature dependence of spin-lattice relaxation time of ^{23}Na

Table 1 Electric quadrupole constant e^2qQ and asymmetry parameter η

	90 K	300 K
Site I & III		
$e^2qQ/h\nu_n$	930 G	440 G
η	0.52	0.30
Site II		
$e^2qQ/h\nu_n$	420 G	430 G
η	0.46	0.78

electric quadrupole parameters at 90K and 300K are listed in Table (1).

The electromagnetic properties of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ are determined by the behaviors of the V^{4+} ions, so that we expect that EPR measurement brings us crucial informations. EPR results were published by Friedrich et al., who measured the temperature dependence of the spin-susceptibility, g-value and the linewidth in a certain crystal orientation [4]. In the present work, we concentrate on precise measurements of the anisotropy of g-value and linewidth. The results are shown in Figs.(4) and (5).

The observed g-value is appreciably anisotropic and the derived principal values at 300K are

$g_x = 1.936 \pm 0.002$, $g_y = 1.957 \pm 0.002$ and $g_z = 1.982 \pm 0.002$, where X- and Y-axis lie in the ac-plane and Z-axis corresponds to the b-axis. An angle between X- and the crystallographic a-axis is $67^\circ \pm 2^\circ$. The principal axes X, Y and Z coincide to those of the distorted octahedron of oxygen atoms surrounding V_1 sites, as shown in Fig.(6), which suggests that V^{4+} ions primarily occupy the V_1 position.

On the basis of structural data by Wadsley [5] that the vanadium atoms are nearly octahedrally surrounded by oxygen atoms, Goodenough considered the inter-atomic spacing between V and O atoms, and concluded that the 3d-electrons in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ are localized to the d_{yz} -orbitals at the site I. We found that the d_{yz} -state does not explain the experimental relative magnitude of $2^> g_z > g_y > g_x$, as far as the energy levels of d states are much lower than those of d_y states. The only level configuration, which can explain the ob-

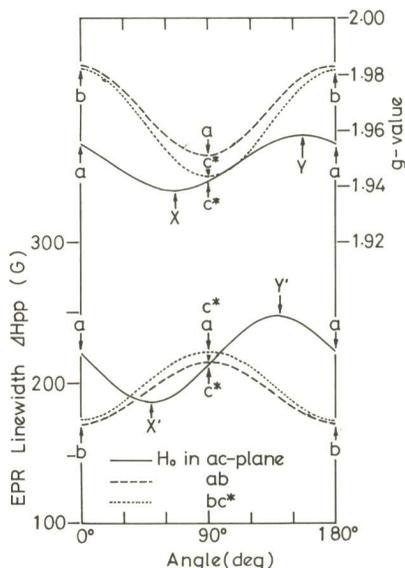


Fig. 4 Angular dependence of g-value and peak-to-peak width of EPR absorption derivative at 300K

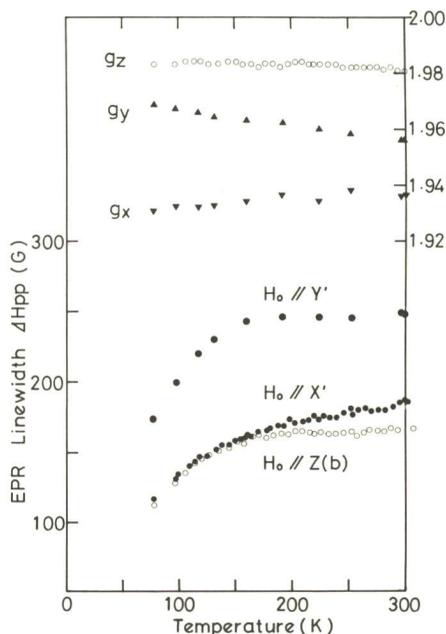


Fig. 5 Temperature dependence of principal values of g-tensor and EPR linewidth

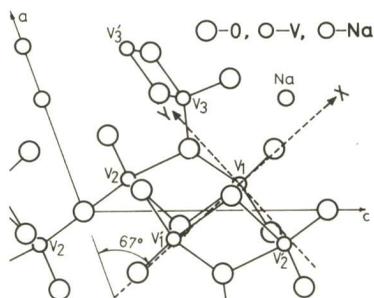


Fig. 6 Crystal structure in the vicinity of V_1 site projected onto an ac -plane and principal axes of g -tensor

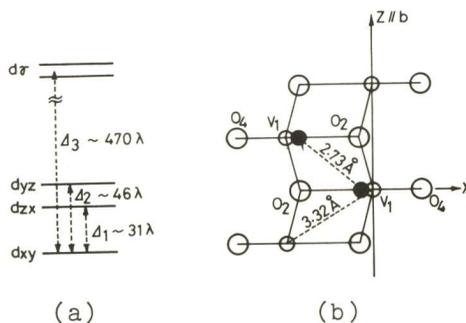


Fig. 7 (a) Level configuration of 3d-states which can interpret the observed anisotropy of g -value and (b) displacement of V_1 position proposed in text

served anisotropy of g -value, is shown in Fig.(7-a), where the ground state is d_{xy} instead of d_{yz} . This configuration contradicts with the crystalline field calculation based on a point-charge model, and the consideration of the covalent admixture of p -electrons of oxygen ions cannot improve this situation. It is found that the level configuration shown in Fig.(7-a) can be obtained qualitatively, if the V^{4+} ion in the V_1 site lies nearly at the center of the distorted octahedron. Thus we suppose rather boldly that the V_1 position shifts along the negative X -direction about ~ 0.4 Å only when this site is occupied by V^{4+} ions.

If this distortion takes place in the adjacent V_1 position simultaneously, the nearest neighbor distance between V^{4+} - V^{4+} pair is reduced to be ~ 2.73 Å (Fig.(7-b)). Recently, Chakraverty et al. [6] proposed a new pairing state, named as 'bipolaron', which is considered as localized Cooper pair in the limit of large electron-phonon coupling, such as the strain induced coupling. The reduction of the pair distance may be related to this kind of attractive force.

The dipolar field for a spin-pair with a distance of 2.73 Å should be narrowed by the hopping motion of 3d-electrons with a correlation time of 4×10^{-11} sec, as expected from NMR measurements, and give Lorentzian line with a halfwidth ~ 350 G, apart from an angular dependent factor. This is sufficient in magnitude to explain the observed linewidth.

References

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