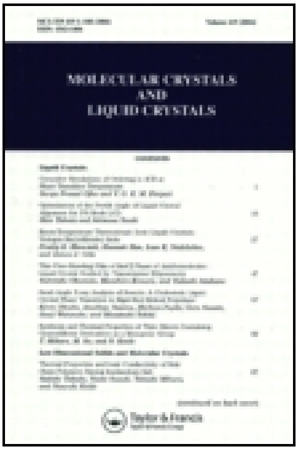

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Mobile Bipolaron In Quasi-1-D Conductor Vanadium Bronzes

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Version of record first published: 20 Apr 2011.

Mol. Cryst. Liq. Cryst. 1985, Vol. 121, pp. 121-124
0026-8941/85/1214-0121/$10.00/0

MOBILE BIPOLARON IN QUASI-1-D CONDUCTOR VANADIUM BRONZES

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Abstract The existence of the characteristic bound state of BIPOLARON (a dimerized electron pair of up and down spins on the near neighbour sites) was established by NMR and X ray diffraction measurements in the quasi-1-d conductor $M_xV_2O_5$(M= Na,Ag,Li,Cu, and Pb). On the basis of the results of EPR and NMR relaxation, the observed high electrical conductivity along the 1-d axis is interpreted as the COLLECTIVE MOTION of BIPOLARONS. These characteristic properties are discussed with the strong electron-phonon interaction of the rather well localized small polarons in the 3d vanadium bronzes, which is different from the 4d molybdenum bronzes.

There are two groups of quasi-1-d conductors. One has a free electron system occupying metallic conduction band and the other a localized electron system having an ionic character. Phenomena of Peierls transition, dynamics of charge density wave, et al. have been investigated on the materials belong to the former group. The unique characteristics of the latter group is the strong electron-phonon interaction. In ionic crystals, the number of optical phonons which clothe an electron are half of its polarizability and about more than one order of magnitude larger than that of usual superconducting metals, so a polaron is expected. In this sense, present subject of vanadium bronze system has the uniqueness of the STRONG ELECTRON-PHONON INTERACTION and HIGH DENSITY of POLARONS. In Table 1 we show the comparative features between 3d,4d,5d transition metal bronze systems.

BIPOLIRON

Recently as the results of strong electron-phonon interaction, the new characteristic bound states are proposed theoretically:
(1) Electron pairing in real space by Anderson[1], and Rice et al.[2] for amorphous semiconductor and $BaBiO_3$ respectively,
(2) A pair of up and down spin on near neighbour site (BIPOLARON) by Chakraverty et al.[3] for $Na_xV_2O_5$(Na v.b.). By using resonance[4~8] and X ray diffraction techniques, we have shown the microscopic evidences of the bipolaron in Na v.b. and the other v.b. system. The susceptibility maximum phenomenon, that is the manifestation of

the spin-singlet ground state, is observed by the Knight shift of ^{51}V NMR as shown in Fig.1. X ray diffraction measurements revealed that the spin-singlet ground state is accompanied with the small displacement of vanadium ions and the long range ordering of bipolaron(Fig.2) occurs below 200 K as shown in Fig. 3[9~10].
The observed conductivity of Na v.b. along 1-d axis is $10^2 \Omega^{-1} cm^{-1}$ at 300 K and two order of magnitude larger than that of perpendicular direction. Its temperature dependence is semiconductor-like. The high and anisotropic conductivity of Na v.b. is considered to be originated to the electron hopping motion in the quasi-1-d zigzag chains of vanadium ions. The detailed experimental results of the anisotropic EPR line width as a function of temperature are well understood as the extreme narrowing limit of the hyperfine interaction between ^{51}V nuclei and the dipole-dipole interaction between electron spins. It is found that the characteristic time of the electron hopping motion τ_c is 1.2×10^{-11} sec..
Using the formula of diffusive hopping conductivity given as

$$\sigma T = \frac{N_{/\!/} e^2 l_{/\!/}^2}{k_B \tau_c} e^{-\delta_{/\!/}/T} \qquad (1).$$

We found that the observed high conductivity along 1-d axis can not be understood without using $N_{/\!/} = 24$ bipolarons and $\delta_{/\!/} = 574$ K, since $l_{/\!/} = 3.61$ A, $\tau_c = 1.2 \times 10^{-11}$ sec.. In Fig. 4, the logarithmic plots of the product of temperature and conductivity are shown. This result means that many bipolarons move at the same time collectively and the domain size is about 200 A corresponding to the coherence length obtained by X ray diffraction. Thus we may conclude that the obtained activation energy $\delta_{/\!/} = 0.049$ eV is the pinning energy of domain wall motion in Na v.b..

ELECTRON-PHONON INTERACTION

We found that the bipolaron moves one lattice distance of 3.6 A along the i-d axis with τ_c of 1.2×10^{-11} sec.. This indicates that the effective velocity of bipolaron is 3×10^3 cm/sec., about orders of 5 smaller than the usual Fermi velocity of electron in metal. It may be said that the effective mass of bipolaron is orders of 5 heavier than free electron mass. The effective mass in electron phonon coupled system was obtained by Lee-Rice-Anderson[11] as

$$M^*/m_0 = 1 + \frac{1}{\lambda}\left(\frac{2\Delta}{\hbar\omega_q}\right)^2 \qquad (2),$$

where $q = 1/2\ b^*$, $\omega_q = v_{b,p} \times q$ (phonon energy), $2\Delta = 300$ K(binding energy) and $M^*/m_0 = 10^5$, we estimate the electron-phonon coupling constant $\lambda = 1$. Knowing λ and the experimentally obtained value of $n(E_f) = 10^{-4}$ state /eV, we got the magnitude of electron-phonon coupling $g_q = 1$ eV in vanadium bronze system. Therefore, we can conclude that the strong electron-phonon interaction is realized in these systems as expected previously. In Table 2, several characteristic properties are given in vanadium bronze systems.

REFFERENCES

1. P.W. Anderson, Phys. Rev. Lett. 34 953 (1975)
2. T.M. Rice, and L. Sneddon, Phys. Rev. Lett. 47 689 (1981)
3. B.K. Chakraverty, M.J. Sienko, and J. Bonnerot, Phys. Rev. B17 3781 (1978)
4. K. Maruyama, and H. Nagasawa, J. Phys. Soc. Jpn 48 2159 (1980)
5. M. Onoda, T. Takahashi, and H. Nagasawa, phys. stat. solidi b109 793 (1982)
6. M. Onoda, T. Takahashi, and H. Nagasawa, J. Phys. Soc. Jpn 51 3868 (1982)
7. M. Onoda, and H. Nagasawa, J. Phys. Soc. Jpn 52 2231 (1983)
8. T. Erata, and H. Nagasawa, J. Phys. Soc. Jpn 52 3652 (1983)
9. Y. Kanai, S. Kagoshima, and H. Nagasawa, J. Phys. Soc. Jpn 51 697 (1982)
10. Y. Kanai, S. Kagoshima, and H. Nagasawa, Synthetic Metals 9 369 (1984)
11. P.A. Lee, T.M. Rice, and P.W. Anderson, Solid State Commun 14 703 (1974)

Table 1 Comparison of characteristics between transition metal bronzes

Bronzes	*Electronic States*	*Structural Condition*	*Physical Characteristics*
W-Bronzes ex. $Na_{0.3}WO_3$	large polaron (delocalized 5d electron)	3- dimensional metal	Superconductivity
Mo-Bronzes ex. $K_{0.3}MoO_3$	middle size polaron (4d electron)	quasi-1-dimensional metallic	C. D. W.(Metal) Non-Linear-Transport Phenomena
V-Bronzes ex. $Na_{0.4}V_2O_5$	small polaron (localized 3d electron)	quasi-1-dimensional ionic character	C. D. W. (Bipolaron) Strong Electron-Phonon Interaction

Table 2 Bipolaron in β-$M_xV_2O_5$ systems

M^{n+}	x	T_c (K)	$q^{satellite}$	Binding Energy (K)
Na^{1+}	0.40	200	(0,0.5,0)	170
Ag^{1+}	0.38	210	(0,0.5,0)	200
Li^{1+}	0.53	220 190 170	(0,0.44~0.47,0) (0,0.43,0.125) (0,0.5,0.5)	200
Cu^{1+}	0.26< x <0.62	205(x=0.33) 215(x=0.40) 210(x=0.48) 170(x=0.48) 250(x=0.54) 280(x=0.63)	(0,0.35,0) (0,0.33,0) (0,0,0.15) (0,0.26,0) (0,0,0.15) (0,0,0.15)	300 300
Pb^{2+}	0.18< x <0.52			200~500 (x dependent)

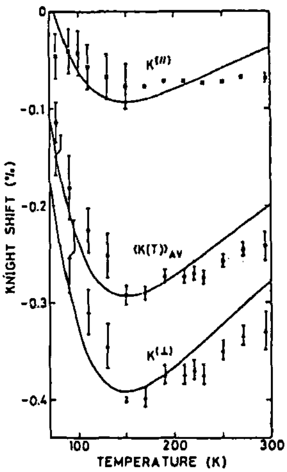

Fig. 1 Temperature dependence of Knight shift.

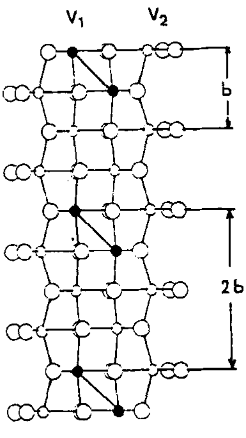

Fig. 2 Bipolaron ordering in $Na_{0.40}V_2O_5$

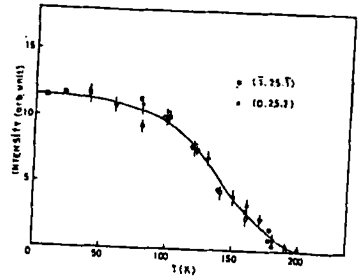

Fig. 3 Temperature dependence of satellite intensity in $Na_{0.40}V_2O_5$

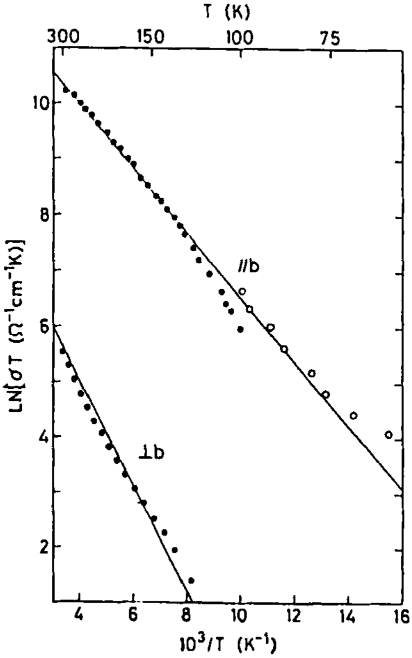

Fig. 4 Logarithmic plot of the products of temperature and the conductivity parallel and perpendicular to the b axis as a function of the inverse of temperature. Closed and open circles indicate the D.C. and the microwave conductivity results, respectively. Solid lines show the calculated results obtained by using the formula and parameters given in text.