FIG. 1. Part of photometric record showing six components of CuBr 0,0 band.

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BOND-POLARIZABILITY DERIVATIVES OF SOME ORGANOMETALLIC COMPOUNDS

BOND and molecular polarizabilities as well as bond polarizability derivatives provide valuable information about the chemical bonds. On the basis of quantum mechanical models, several investigators developed a number of ways to compute the bond and molecular polarizabilities and bond polarizability derivatives for many ions, atoms and molecules. Among the different potential models, the delta function model of the chemical binding initiated by Frost[1]

and developed by Lippincott[2] is considered as most widely acceptable. Lippincott and Stutman[3] extended the semi-empirical delta-function model in the calculation of bond and molecular polarizabilities for various diatomic and polyatomic molecules and obtained good agreement between calculated and experimental values. In recent years, this model has been successfully applied by a number of workers to compute bond and molecular polarizabilities. Using delta-function model, Fontal and Spiro[4], Lippincott and Nagarajan[5] and Long and Plane[6] have devised methods for calculating the bond polarizability derivatives. On account of the availability of Laser sources in Raman spectroscopy, a thorough study of the aforesaid data for different molecules is demanded. Therefore, the study has been extended for some organometallic compounds. The importance in undertaking such investigations is that firstly, bond polarizability derivatives obtained here would be much useful for interpretation of the results of (1) experimental refractive indices and (ii) experimental absolute Raman intensities and secondly to select the most suitable method out of the three. The molecules under present study have been taken from the references[7-9].

The required data for such computations are the molecular structural data, electronegativities of the elements on Pauling scale, delta function strengths and atomic polarizabilities. The values are taken

TABLE I

Polarizability derivative $(\partial \bar{a}/\partial R$ in $Å^2)$ for some molecules

Molecule	Bond	Method			Exp.
		FS	LN	LP	
[(CH₃)₃ Pt] (OH)₄	C–Pt	2·454	2·885	3·657	2·03
(CH₃)₃ GeMn (CO)₅	Ge–Mn	2·821	3·791	5·195	2·97
(CH₃)₃ GeRe (Co)₅	Ge–Re	3·328	4·604	6·275	2·74
(CH₃)₃ SnMn (Co)₅	Sn–Mn	3·731	4·938	6·987	3·07
(CH₃)₃ SnRe (Co)₅	Sn–Re	3·912	6·044	8·037	3·79
(H₂O)₂ Hg²⁺	Hg–Hg	4·179	7·808	10·088	4·65
(CH₃)₆ Ge₂	C–Ge	1·927	2·629	2·922	1·81
	Ge–Ge	2·637	4·559	4·383	2·20
(CH₃)₆ Si₂	C–Si	1·428	2·531	3·676	1·82
	Si–Si	1·825	3·655	4·202	1·69
(C₆H₅)₆ Sn₂	C–C	0·789	1·506	1·948	
	Sn–Sn	5·488	6·844	6·786	3·89
	C–Sn	2·379	3·204	3·617	2·93
(CH₃)₂ GeH₂	Ge–C	1·841	2·512	2·791	
	Ge–H	1·040	1·763	2·838	
(CH₃)₃ GeCl	Ge–C	1·813	2·473	2·748	
	Ge–Cl	2·878	2·148	1·902	
(CH₃)₃ GeBr	Ge–C	1·801	2·458	2·732	
	Ge–Br	4·014	4·275	4·079	

from references[10–13]. The bond lengths under present investigation are taken from references[7–9,4].

The bond-polarizability derivatives calculated following Fontal and Spiro (FS), Lippincott and Nagarajan (LN) and Long and Plane (LP) for the molecules under present study are presented in Table I. The experimental values[7–9] are also included in the last column of the same table. A comparision of the experimental values with the computed values shows that in most of the cases Fontal and Spiro method gives better results. Following are some important conclusions drawn on the basis of the results of Fontal and Spiro.

In organometallic compounds the bond polarizability, derivatives increases in the order

$$\bar{a}'_{Si-C} < \bar{a}'_{Ge-C} < \bar{a}'_{Sn-C}$$
$$\bar{a}'_{Ge-H} < \bar{a}'_{Ge-Cl} < \bar{a}'_{Ge-Br}$$
$$\bar{a}'_{Si-Si} < \bar{a}'_{Ge-Ge} < \bar{a}'_{Sn-Sn}$$
$$\bar{a}'_{Ge-Mn} < \bar{a}'_{Ge-Re} < \bar{a}'_{Sn-Mn} < \bar{a}'_{Sn-Re} < \bar{a}'_{Hg-Hg}$$

These trends are in good agreement with all previous results of this kind. The first trend can be explaind on the basis of nature of electronegativity difference of the bonds while the last trends can be explained on the basis of the fact that the interaction between heavier atoms is less, therefore, bond polarizability derivative will be more.

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STUDIES ON THE ELECTRICAL PROPERTIES OF MAGNESIUM METAVANADATE

MAGNESIUM METAVANADATE is one of the members of a series of compounds, MV_2O_6 where M = Mg, Co, Zn, Ca, Hg, etc., having brannerite[1] ($ThTi_2O_6$) crystal structure.

The reports[2-6] on the $MgO-V_2O_5$ system indicated a stable phase with composition MgV_2O_6 and the crystal structure studies[7] of the phase showed space group C2/m of monoclinic symmetry. A recent investigation[8] of X-ray diffraction and D.T.A. of MgV_2O_6 synthesised under the conditions mentioned elsewhere confirmed a structural transition at 833 K, both polymorphs having brannerite crystal structure.

Except these phase studies and the studies on the crystal structure no other information is available concerning the solid state properties of MgV_2O_6 which has initiated this investigation.

Experimental

A new MgV_2O_6 phase is synthesised by solid state reaction as discribed elsewhere and matched with earlier reports[3,4]. The DC electrical conductivity (σ) of the polycrystalline magnesium metavanadate phase was measured between 300–1000 K by two probe technique. The sample was in the form of a sintered compact (above 85% packing density) of 18 mm diameter and thickness of 2 mm. The Seebeck coefficient (a) of the compound was measured between 300–1000 K by integral method. The ESR spectrum was recorded in a varian x-band instrument operating at 8·82 GHz with DPPH as marker.

Results and Discussion

Stoichiometric MgV_2O_6 is an electrical insulator. However XRD σ and a results of the present work showed that the compound synthesised retained the gross monophasic MV_2O_6 (M is a divalent cation) crystal structure[1] but having nonstoichiometric composition and exhibiting n-type semiconduction. The transport behaviour of magnesium metavanadate is reminiscent of hopping mechanism of conduction. The temperature dependence of σ follows the relationship $\log_{10} \sigma T = \log_{10} \sigma_0 - \Delta G_0^*/2 \cdot 303 KT$ where ΔG_0^* is the free energy of activation for conduction. This is evidenced by the linearity of $\log_{10} \sigma T$ versus $1/T$ plot (not shown) and the temperature independence of Seebeck coefficient, a. The sign of a is negative and temperature independent, indicating constant number of charge carriers. This is further confirmed by ESR measurement of the phase at 300 K which showed a signal at $g = 1 \cdot 96$ with a narrow line width. The narrow line width at 300 K pointed out (a) localisation of the d-electron (V^{4+}) at the lattice sites and (b) hopping mechanism of the d-electron between the equivalent vanadium sites.

In magnesium metavanadate, anion vacancies occur leaving behind two electrons per $\frac{1}{2}$ molecule of oxygen leaving the lattice; in other words, the metavanadate can be represented as $Mg^{2+} V_{2-2x}^{5+} V_{2x}^{4+} O_{6-x}$ for small value of x under conditions of its synthesis indicating the reduction of a small amount of V^{5+} to V^{4+}. Thus it becomes established that MgV_2O_6 exhibits n-type conduction due to electron hopping on equivalent $V^{4+} - V^{5+}$ sites in the lattice.

TABLE I

Electrical transport data for MgV_2O_6

Compound	Temperature	Sign of Seebeck coefficient a	Electrical conductance σ, Ohm^{-1} Cm^{-1}	Activation energy ΔG^* (eV)
a-MgV_2O_6	300–830 K	n-type	10^{-6} to 10^{-3}	0·25
β-MgV_2O_6	833–1000 K	n-type	10^{-4} to 10^{-3}	0·50