The Chemical Bonds in $Me\mathrm{Sb_2O_4}$ (Me = Mn, Ni, Fe, Zn) Isomorphous Compounds: Thermal Expansion, Force Constants, Energies

J. R. GAVARRI AND R. CHATER

Laboratoire de Chimie Physique du Solide, U.A. No. 453 au CNRS, Université Paris XIII et Ecole Centrale des Arts et Manufactures, Chateny-Malabry, 92290 France

AND J. ZIÓŁKOWSKI

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, 30-239 Poland

The various chemical bonds (Me–O, Sb–O) in the $Me\mathrm{Sb_2O_4}$ isomorphous compounds (Me = Mn, Ni, Fe, Zn) are characterized by four quantities: the interatomic distance (r_{ij}), the force constant (f_{ij}), the thermal expansion ($\alpha_{ij} = 1/r \; dr/dT$), the bond energy. Using structural evolution data (neutron diffraction) and Raman infrared spectroscopic studies at low temperature (5–300 K), it has been possible to connect the various r_{ij}, f_{ij}, and α_{ij} quantities with bond energies; such energies have been calculated using a simplified pair potential model $U(r) = Ar^{-m} - Br^{-n}$; calculated force constants and thermal expansions have been derived from the derivatives d^2U/dr^2 and d^3U/dr^3. For each $Me\mathrm{Sb_2O_4}$ compound lattice energies (E_r) are then proposed. Using a new empirical bond-length–bond-energy method [J. Ziółkowski, *J. Solid State Chem.* **57**, 269 and 291 (1985)] dissociation energies of Me–O and Sb–O bonds have been evaluated for each $Me\mathrm{Sb_2O_4}$ compound. The total calculated dissociation energy $D(Me\mathrm{Sb_2O_4} \rightarrow Me^\circ + 2\,\mathrm{Sb}^\circ + 40^\circ)$ is then compared to the lattice energies E_r obtained from the first method. The $|E_r|$ and D values are respectively about 1080 and 790 kcal · mole^{-1}; the difference is directly linked with the ionic character of Me–O bonds. © 1988 Academic Press, Inc.

I. Introduction

The isostructural antimony oxides $Me\mathrm{Sb_2O_4}$, with Me = Mn, Ni, Fe, Zn, have been extensively studied (*1–6*) using X-ray and neutron diffraction at low temperature. These crystallographic studies have allowed us to correlate the structural evolutions with various physical properties such as magnetism, elasticity, or specific heat. Recently, new magnetic and structural data on $\mathrm{MnSb_2O_4}$ have been reported (*7*).

We have shown that, in the case of polycrystalline samples, the elasticity tensor might be investigated by connecting anisotropic vibration amplitudes with anisotropic thermal expansion of tetragonal cells in the temperature range 5–300 K.

In the present work, we try to evaluate individual bond energies for the $Me\mathrm{Sb_2O_4}$ compounds using two different methods.

(1) The first method consists of evaluating bond energies from simple pair potentials $U(r) = Ar^{-m} - Br^{-n}$ which have been
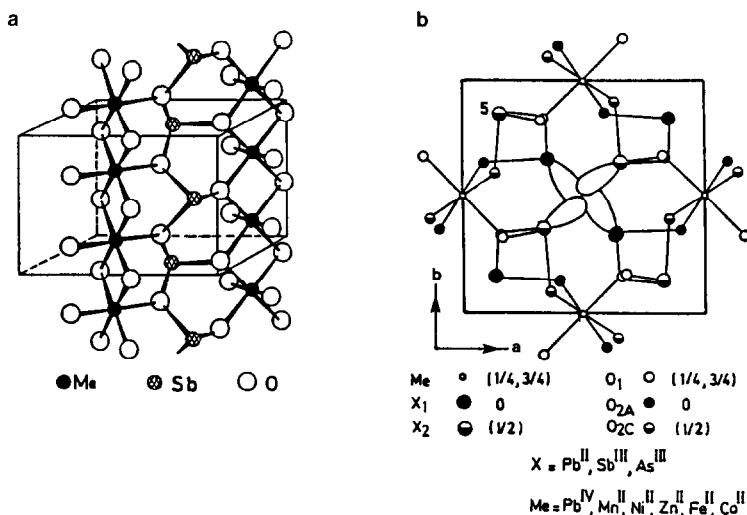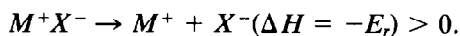
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FIG. 1. (a) Structure of $Me\mathrm{Sb}_2\mathrm{O}_4$: the linear chains of octahedrons are represented. (b) Projection in the (a, b) plane: lone pairs of Sb^{3+} atoms are mentioned.

calibrated using thermal expansion data and vibrational force constants. The definition of such energies corresponds to the dissociation:

$$M^+X^- \to M^+ + X^-(\Delta H = -E_r) > 0.$$

(2) The second method consists of evaluating individual bond energies ($E_f < 0$) corresponding to the classical dissociation energy of bonds (8, 9):

$$M^+X^- \to M^\circ + X^\circ(\Delta H = D = -E_f).$$
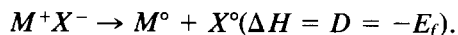
The relation between E_f and E_r is given by

$$E_f = E_r + \Sigma_{ij}(I_i + A_{e(j)}),$$

where I_i and $A_{e(j)}$ are, respectively, the so-called ionization energies of cations and electron affinities of anions.

Structural Data

At room temperature, the $Me\mathrm{Sb}_2\mathrm{O}_4$ antimony oxides crystallize in the tetragonal system with a space group $P4_2/mbc$ (D_{4h}^{13}) and $Z = 4$. The effective formula should be written taking into account lone pairs E of Sb^{III} atoms: $Me\mathrm{Sb}_2\mathrm{O}_4E_2$. Such lone pairs

are "in contact" in the structure with a volume comparable to that of oxygen atoms (10, 11). The structural analyses were carried out on polycrystalline samples using first X-ray then neutron diffraction (1–6).

Figure 1 represents the structure of the $Me\mathrm{Sb}_2\mathrm{O}_4$ antimony oxides: octahedron chains $(Me\mathrm{O}_6)_n$ are aligned in the c direction and bound together by O–Sb–O bridges. Each octahedron is composed of 4 Me–O_2 bonds and 2 Me–O_1 bonds. The distorted tetrahedron SbO_3E are composed of 2 Sb–O_1 (2.01 Å) bonds and one Sb–O_2 bond (1.94 Å).

Table I recalls the various interatomic distances which have been calculated from crystallographic determinations of atomic coordinates and cell parameters.

II. Experimental Data

II.1. Neutron Diffraction

The experimental thermal expansion of bonds can be obtained from complete structure determination; however, in the case of

TABLE I

INTERATOMIC DISTANCES AND THERMAL EXPANSION OF BONDS OF MnSb$_2$O$_4$,
NiSb$_2$O$_4$, ZnSb$_2$O$_4$, Pb$_3$O$_4$, SnPb$_2$O$_4$

Distances (Å) dilatation ($\times 10^6$ K)	MnSb$_2$O$_4$	NiSb$_2$O$_4$	ZnSb$_2$O$_4$	Pb$_3$O$_4$*	SnPb$_2$O$_4$*
Me–O$_1$	2.214	2.083	2.181	2.14	2.05
$\bar{\alpha}$(5–300 K)	29	12.6	30	8	12
Me–O$_2$	2.132	2.051	2.073	2.19	2.09
$\bar{\alpha}$(5–300 K)	−0.3	4	0	0	3.8
Sb–O$_1$(Pb^{II}O$_1$)*	2.013	1.999	2.002	2.21*	21*
$\bar{\alpha}$(5–300 K)	−3.2	−4.7	3		2.32*
Sb–O$_2$(Pb^{II}O$_2$)*^{a}	1.953^a	1.930	1.935	2.33*	17
$\bar{\alpha}$(5–300 K)	13.9	21	22	16	
O$_2^{(0)}$–O$_2$(1/2)	3.030	2.972	2.980		
$\bar{\alpha}$(5–300 K)	−8.5	0.2	0.2		
O$_1$(1/4)–O$_1$(3/4)	3.001	2.954	2.961		
$\bar{\alpha}$(5–300 K)	7.5	1.00	0.0		

^{a} In Ref. (7), this Sb–O distance is equal to 1.866 Å; such a strong discrepancy might be due to the experimental conditions. The neutron diffraction data reported by these authors were collected in a limited diffraction angle range ($2\theta < 80°$) while all our results reported here have been obtained from the high angle resolution diffractometer D1A of ILL (Grenoble) in the angle range 0–160° 2θ.

* Ref. (1).

oxides, neutron diffraction is necessary for obtaining accurate oxygen atom coordinates, and, as a consequence, for obtaining accurate variations of Me–O, Sb–O bonds vs temperature.

The "macroscopic" thermal expansion of the tetragonal cells ($\alpha_a = (1/a)(\Delta a/\Delta T)$ and $\alpha_c = (1/c)(\Delta c/\Delta T)$) is obtained from both X-ray and neutron diffraction in the range 5–300 K.

Using the D1A diffractometer of ILL (Grenoble) (11) many experimental data have been recorded at low temperatures. The diffraction patterns have been interpreted using the Rietveld procedure (12, 13, 14) which is well adapted to the structural evolution studies vs temperature. Cell parameters can be refined at each temperature with a high relative accuracy: standard deviations $\sigma(a)/a$, $\sigma(c)/c$ of about 5×10^{-5} can be obtained. Atomic coordinates can be evaluated with standard deviations of 1 to 5×10^{-4}. These quantities allow determination of the variations of interatomic distances with a reasonable precision. The results concerning thermal expansions of the Me–O$_1$, MeO$_2$, SbO$_1$, SbO$_2$ chemical bonds are conditioned by site symmetries. The Wyckoff positions are in the space group $P4_2/mbc$:

$$Me^{II}(d): 0 \tfrac{1}{2} \tfrac{1}{4}$$

$$O_1(g) : x, \tfrac{1}{2} + x, \tfrac{1}{4}$$

$$O_2(h) : x, y, 0$$

$$Sb^{III}(h): x, y, 0.$$

As a consequence, the O$_2$ and Sb atomic positions are refined with a smaller accuracy.

Generally in the case of ionocovalent compounds, the thermal expansions of bonds $\alpha_l = \Delta d/d\Delta T$ are expected to be of about 0–30 $\times 10^{-6}$ K^{-1}; in the case of our studies, absolute errors are of about 5 $\times 10^{-6}$ K^{-1}. As a consequence, for small expansions less than 5 $\times 10^{-6}$ K^{-1} the values are uncertain.
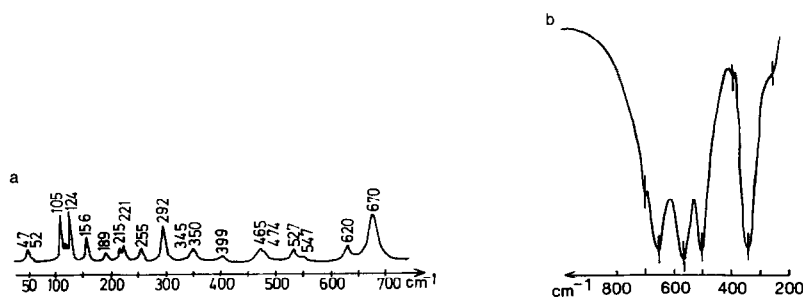
FIG. 2. Vibrational studies. (a) Raman spectrum of $MnSb_2O_4$. (b) Infrared absorption spectrum of $MnSb_2O_4$.

Table I delivers the interatomic distances and thermal expansions in the range 5–300 K. Generally the values obtained in the restricted temperatures range 100–300 K are expected to be higher because of the weakness of expansions at very low temperatures (0–50 K); however, experimental accuracy on variations Δd is too weak to deliver significant indications.

It is important to note that the Me–O bonds present high α_l values while the Sb–O_1 bonds present very small α_l values; a surprising result is observed for the Sb–O_2 bonds with high α_l values as compared to that of Sb–O_1, in spite of the fact that the first mentioned bond is shorter. We used these experimental results to interpret force constants in a previous work (6).

II.2. Raman and Infrared Spectroscopy

The Raman spectra were recorded from a Coderg spectrometer with triple monochromator (Paris 13 University).

The incident radiation was delivered by an Argon laser. The IR spectra were obtained from two types of spectrometers: (i) the Perkin–Elmer spectrometer in the frequency range 200–1000 cm⁻¹; (ii) the Fourier transform interferometer Polytec FIR 30 in the lower frequency range 10–200 cm⁻¹. All the frequency bands were located in the range 10–800 cm⁻¹ (5).

Figure 2 represents one of the Raman spectra (2a) and one of the infrared spectra corresponding to $MnSb_2O_4$: the intensity of

each band is connected with polarizability of bonds, i.e., with covalency.

Force constants. The vibrational analysis allowed us to connect frequencies with individual force constants and interactions (e.g., $\omega(cm^{-1}) = (F/m)^{1/2}$) for the family of isomorphous $MeSb_2O_4$ and $MePb_2O_4$ (Pb_3O_4, $SnPb_2O_4$). Table II delivers the principal force constants which have been refined after a complete force field determination. The computer calculations have been performed according to the programs of Schachtschneider (15) and Bates (16). Such programs are based on the Shimanouchi method (17). Calculations are carried out with the Univac 1110 computer. The previous studies on Pb_3O_4 and $SnPb_2O_4$ of Vigouroux et al. (18) were used in order to obtain coherent results for the isomorphous structures $Me^{IV}Pb_2O_4$ and $Me^{II}Sb_2O_4$. Let us recall that for polycrystalline

TABLE II

FORCE CONSTANTS AND ANGLE RIGIDITY IN
$MnSb_2O_4$, $NiSb_2O_4$, $ZnSb_2O_4$

f (in 10^2 N/m)	Mn	Zn	Ni
fd_1 (Me–O_2)	0.70	0.75	0.84
fd_2 (Me–O_1)	0.53	0.60	0.73
fD_1 (Sb–O_2)	1.70	1.60	1.70
fD_2 (Sb–O_1)	2.00	2.12	2.08
fD_4 (SbE–SbE)	0.05	0.10	0.15
f_γ (O–Sb–O)	0.60	0.45	0.55
f_α (O–Me–O)	0.30	0.30	0.30

materials, it is important to get supplementary informations for good vibrational band attributions; in the present case it was necessary to use the same force field hypotheses for fitting calculated frequencies to observed bands obtained from both Me^{IV}Pb$_2$O$_4$ and Me^{II}Sb$_2$O$_4$ compounds.

The principal results can be summarized as follows:

(1) The force constants of Me^{II}–O bonds are about 50 N/m and weaker than those of Sb^{III}–O bonds (~200 N/m): such differences were expected from the different ionic charges of metal atoms and from the different bond lengths (Table I).

(2) The Me^{II}–O$_2$ bonds are more rigid than the Me^{II}–O$_1$ ones: this feature is congruent with the different lengths ($d(Me$O$_1)$ > $d(Me$O$_2)$) and with the thermal expansion data obtained from diffraction experiments ($\alpha(Me$O$_1)$ > $\alpha(Me$O$_2)$).

(3) In the case of Sb–O bonds, the various results seem to be paradoxical: the Sb–O$_2$ bonds appear to be less rigid than the Sb–O$_1$ bonds which is consistent with the diffraction results ($\alpha(\text{Sb}$O$_2)$ > $\alpha(\text{Sb}$O$_1)$) but remains in contradiction with the bond length values, $d(\text{Sb}$O$_2)$ < $d(\text{Sb}$O$_1)$. This apparent contradiction will be explained later.

In addition the qualitative analysis of Raman intensities seems to argue in favor of strong covalence for Sb–O bonds and of ionic character for Me–O bonds. This last feature might be in full agreement with the observed magnetic moments at 5 K in the case of Ni, Mn, Fe compounds (3, 4): each observed value is quite congruent with Me^{2+} ions in the HS state.

III. Principles and Results of the Calibrated Pair Potential Method: Lattice Energy

III.1. Models

The pair potential chosen in this approach is that of Gruneisen,

$$U(r) = Ar^{-m} - Br^{-n}, \qquad (1)$$

where r is the interatomic distance for chemically bound atoms; A and m characterize the repulsive interactions, B and n the attractive part which can be due either to pure coulombian anion–cation attraction or to covalent, dipolar, metal interactions.

The minimum of potential is reached for $U'(r) = 0$, i.e., for

$$(r_0)^{m-n} = (mA)/(Bn), \qquad (2)$$

where r_0 is the equilibrium distance (in the absence of any vibration).

The force constants related to stretching vibrational modes can be calculated as follows:

$$f = U''(r = r_0) = (d^2U)/(dr^2)r = r_0.$$

Using the expansion of potential (1) one obtains:

$$f = U'' = (m - n) \times Br^{-(n+2)} \times n. \quad (3)$$

In the case of coulombian interactions, one obtains $n = 1$ and $B = (4\pi\varepsilon_0)^{-1} \cdot ZZ' \cdot \beta e^2$, where β is the Madelung term; it results in

$$f = (m - 1)\beta \, ZZ'(230.4 \times 10^{-30})r^3, \quad (3')$$

where Z and Z' are the effective charges (+ and −) of ions; if r is expressed in meter, f is in Newtons per meter.

The thermal expansion of bonds is due to the anharmonic terms in potential and principally, for intermediate temperatures ($T \sim \Theta$ Debye), to the third derivative U''' ($r = r_0$),

$$\alpha_l = -\frac{k_B}{2r_0}\frac{U'''}{(U'')^2} = (m + n + 3) \cdot \frac{k_B}{2r_0^2 \cdot f}$$

$$= \frac{m + n + 3}{2(m - n)} \cdot \frac{r_0^n}{B \cdot n} \cdot k_B, \quad (4)$$

and with the coulomb approach,

$$\alpha_l = \frac{m + 4}{2r_0^2 \cdot f} \cdot k_B$$

$$(k_B = 1.38.10^{-23} \text{ J}). \qquad (4')$$

Finally, the bond energy (for one atomic pair) can be written as

TABLE III

BOND ENERGY: $U(r) = Ar^{-m} - Br^{-n}$

	r (Å)	$\bar{\alpha} \times 10^6$ (Neutrons)	$f \times 10^{-2}$ (N/m) (Spectro)	m^a	$ZZ'\beta = (4\pi\varepsilon_0 e^{-2} \cdot B)^b$	$(-U(r_0))$ in kcal/mole
Mn–O$_1$	2.21	29		7	0.40	52.5
Zn–O$_1$	2.18	30		7	0.39	50.7
Ni–O$_1$	2.08	13	$\langle 0.52 \rangle^e$	7	0.34	46.3
Fe–O$_1{}^c$	2.20	18		7	0.40	51.5
Mn–O$_2$	2.13	0.		7^d	0.49	65.2
Zn–O$_2$	2.07	10.6	$\langle 0.70 \rangle$	7^d	0.45	61.6
Ni–O$_2$	2.05	4		7^d	0.44	60.8
Fe–O$_2{}^c$	2.11	0.		7^d	0.48	64.4
Sb–O$_1$	2.01	−3.2	$\langle 2 \rangle$	9^d	0.88	128.7
Sb–O$_2$	1.95	14	$\langle 1.7 \rangle$	9	0.68	102.5

^{a} Only one mean m value is used for Me–O bonds and one for Sb–O bonds.

^{b} $ZZ'\beta$ is related to the Madelung contribution for pure ionic bonds.

^{c} The values for Fe–O bonds have been extrapolated from vibrational results of the other compounds.

^{d} Postulated values.

^{e} $\langle \ \rangle$ indicates averages.

$$U(r_0) = B[(1 / m) - 1/n)] \times n/(r_0)^n < 0, \quad (5)$$

or in the case of pure coulomb interactions as

$$U(r_0) = (230.4 \times 10^{-30}) \cdot \beta \cdot ZZ' \cdot [(1 / m) - 1](1/r). \quad (5')$$

Four data are needed to calculate the energy $U(r_0)$: B, m, n, and r_0. Only three experimental relations are available: (2), (3), and (4); in other terms, only *two structural data* r_0 and α_1 and *one vibrational data* f are available to characterize the chemical bonds.

So, it is necessary to postulate that, as a first approximation, all bonds can be considered as ionic; with the reasonable hypothesis $n = 1$ it is possible to determine the A, B, m terms and to evaluate the energies of similar bonds for a full set of isomorphic compounds. Relation (4) delivers the m value for each bond; then, using (3) one obtains the B value. Finally the A value (repulsion) is deduced from (2).

Table III delivers the calculated values of $U(r_0)$ for the postulated chemical bonds. These values must be considered as relative values not as absolute effective quantities because of large initial incertitudes due to imprecise thermal expansions. The m values have been fitted after postulating a constant electron core repulsion for Me cations; in addition, due to the various incertitudes the same m values for Sb–O$_1$ and Sb–O$_2$ bonds were assumed. As a result, the B (or $ZZ'\beta$) term is calculated for each bond. Some details are given in Tables III and VIII.

III.2. Lattice Energies

From the individual energies of bonds E_i, it is possible to define a lattice energy as

$$E_r = \sum_i n_i E_i \text{ with } E_i < 0,$$

where n_i is the number of chemical bonds having the same energy E_i. In the case of $Me\text{Sb}_2\text{O}_4$ compounds there are:

2 MeO_1 bonds
4 MeO_2 bonds
4 SbO_1 bonds
2 SbO_2 bonds   (per $MeSb_2O_4$ unit).

Each formula unit is characterized by 12 effective bonds and the energy for 1 $MeSb_2O_4$ unit is

$$E_r = 2E(MeO_1) + 4E(MeO_2)$$
$$+ 4E(SbO_1) + 2E(SbO_2).$$

Table IV presents the lattice energies for the $MeSb_2O_4$ isomorphous compounds (Me = Mn, Ni, Zn, and Fe). In the case of $FeSb_2O_4$, no vibrational data are available, and all evaluations have been carried out after extrapolations of vibrational data of the other isomorphous compounds.

IV. Principles and Results of the Bond-Length–Bond-Energy Method: Lattice Dissociation Energy

In this section we try to determine the dissociation energy D using a different empirical method (8, 9). We present first a brief recall of the general method used to determine energies in the case of $MeSb_2O_4$ compounds.

IV.1. Recall

Recently (8) a new relation linking the length R and the strength S of the individual bond in oxide crystals has been established. First, based on the table of the effective ionic radii of Shannon (19), the linear dependence of the cationic radii r_K on the coordination number K has been observed,

$$r_K = r_0 + aK,   \tag{6}$$

where r_0 may be considered as the radius of free cation. It has also been observed for anions,

$$r'_K = r'_0 + a'K'.   \tag{6'}$$

Second, Eqs. (6) and (6') have been combined with the classical definition of the bond strength introduced by Pauling (23),

$$S = Z/K = Z'/K' = 2/K',   \tag{7}$$

where Z and Z' are valencies of cation and anion, respectively, Z' being equal to 2 for oxides. This results in a new S–R relation

$$S = d \times Z/(R - R_0),   \tag{8}$$

where

$$R_0 = r_0 + r'_0$$
$$d = a + 2a'/Z.$$

Coefficient d was moreover found to be linearly related to r_0 so that

$$d = 0.1177 - 0.0081Z - 0.0347r_0$$
$$- 0.0050Zr_0.   \tag{9}$$

The necessity to choose a standard state for ionic radii and bond strength has been pointed out and argued in (9). Structures of simple oxides of the respective cations at room temperature and at normal pressure have been chosen as standard state at which the sum of the strengths of all bonds around the cation is assumed to be exactly equal to its Z. At this assumption, values of so-called standard radii of free ions r_0 have been determined for various cations on the basis of known structural data and listed in (8). The values of r_0 for numerous cations were found to be negative (in particular r_0 = -0.50 Å was found for H^+). It seems more probable that in the former works on the ionic radii, including (19), the size of oxygen anion was assumed too large and consequently the sizes of cations were forced to be small (even negative). To avoid the negative ionic radii a new scale of the abso-

TABLE IV
LATTICE ENERGY ($-E_r$)

$MnSb_2O_4$	1085
$NiSb_2O_4$	1055
$FeSb_2O_4$	1080
$ZnSb_2O_4$	1068

lute ionic radii (ρ_0, ρ_0') has been proposed in (8), based on the assumption that the radius of proton is equal to the nought. Consequently ρ_0'S for all cations are assumed to be

$$\rho_0 = r_0 + 0.5 \qquad (10)$$

and for anions

$$\rho_0' = r_0 - 0.5. \qquad (10')$$

If this new scale of the absolute ionic radii is used Eq. (8) remains valid, R_0 and d are numerically the same but consequently they should be expressed as

$$R_0 = \rho_0 + \rho_0'$$

$$d = 0.1350 - 0.0056Z$$
$$\qquad - 0.0347\rho_0 - 0.0050Z\rho_0. \quad (11)$$

It has been also shown in (9) that so-defined bond strength [cf. Eq. (8)] is directly proportional to the atomization energy D (dissociation),

$$D_i = E(R_i) = J \cdot S = J \cdot \frac{d \cdot Z}{R_i - R_0}$$
$$= \frac{E_a^\circ}{m} \cdot \frac{d}{R_i - R_0}, \quad (12)$$

where coefficient J was found to be equal to the standard molar atomization energy E_a° of the simple oxide Me_mO_n of the considered cation, producing a bond with oxygen, divided by the number m of cations in the

TABLE V

PARAMETERS ρ_0 AND J USED IN CALCULATIONS
OF THE INDIVIDUAL BOND ENERGIES
IN $MeSb_2O_4$ COMPOUNDS

Ion	ρ_0 (Å)	J (kcal · mole^{-1})
Fe^{2+}Hs	0.785	109.0
Ni^{2+}	0.700	109.8
Mn^{2+}HS	0.888	109.3
Zn^{2+}	0.796	86.9
Sb^{3+}	0.964	79.3
O^{2-}	0.829	—

formal molecule of this oxide and by cation valence Z. Values of J for various cations based on the thermochemical data from literature (20) are listed in (9).

It may be useful to note that Eq. (12) has been rationalized (8) in terms of the Hover model of crystal structure. In this model ions are spherical and r_0 and r_0' or ρ_0 and ρ_0' may be considered as a "hard" part of the ions. They do not touch each other, but they are maintained at distances

$$L = R - R_0 = d \times K \qquad (13)$$

IV.2. Application to the $MeSb_2O_4$ Compounds

In the present paper Eq. (12) is applied to calculate the individual bond energies for the series of the considered $MeSb_2O_4$ compounds, using the values of bond lengths R determined in the former structural works on $MeSb_2O_4$ compounds (1–4). The parameters ρ_0 and J used in calculations are gathered in Table V. Those for Fe^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, and O^{2-} are taken from (8, 9). As for Sb^{3+} the structure of orthorhombic Sb$_2$O$_3$ (21) is taken as a standard one, ρ_0 of Sb^{3+} is found to be 0.964 Å. $J_{Sb^{3+}} = 79.3$ kcal · mole^{-1} is calculated using the thermochemical data from (20) and the heat of the polymorphic transformation of Sb$_2$O$_3$ (cubic → orthorhombic) from (22) (possible inaccuracy of the latter heat has no influence on J as it is covered in the limits of the reasonable rounding of J).

The calculated bond energies in $MeSb_2O_4$ compounds are listed in Table VI.

In Table VII, lattice dissociation energies have been calculated in the same way as $E_r(Ef = \Sigma n_i D_i)$.

V. Discussion

V.1. The Pair Potential Model

In MeO_6 octahedrons, the bond energies $|U(r)|$ are about 50 to 60 kcal/mole; the shortest bonds have the strongest energy.

TABLE VI

BOND LENGTHS AND ENERGIES IN $MeSb_2O_4$
COMPOUNDS AT 5 AND 300 K

T (K)	Bond	R (Å)	$\lvert E_f \rvert$ (kcal · mole^{-1})	Bond	R (Å)	$\lvert E_f \rvert$ (kcal · mole^{-1})
5	Zn–O$_1$	2.1617	28.6	Sb–O$_1$	2.0002	80.7
	Zn–O$_2$	2.0655	34.7	Sb–O$_2$	1.9224	129.2
300	Zn–O$_1$	2.1810	27.6	Sb–O$_1$	2.002	80.0
	Zn–O$_2$	2.073	34.2	Sb–O$_2$	1.935	117.7
5	Ni–O$_1$	2.0752	37.2	Sb–O$_1$	2.0018	80.1
	Ni–O$_2$	2.0486	39.1	Sb–O$_2$	1.9180	133.8
300	Ni–O$_1$	2.0803	36.7	Sb–O$_1$	1.999	81.2
	Ni–O$_2$	2.051	38.9	Sb–O$_2$	1.930	122.0
2	Fe–O$_1$	2.1849	33.9	Sb–O$_1$	1.9933	83.5
	Fe–O$_2$	2.1086	39.1	Sb–O$_2$	1.9329	119.5
300	Fe–O$_1$	2.1962	33.2	Sb–O$_1$	1.9895	85.1
	Fe–O$_2$	2.1084	39.1	Sb–O$_2$	1.9392	114.4
2	Mn–O$_1$	2.1949	38.5	Sb–O$_1$	2.0155	75.1
	Mn–O$_2$	2.1324	44.2	Sb–O$_2$	1.9455	109.6
300	Mn–O$_1$	2.2140	37.0	Sb–O$_1$	2.0136	75.8
	Mn–O$_2$	2.1322	44.3	Sb–O$_2$	1.9534	104.2

Note. $D(SbO_2) > D(SbO_1)$ because of the method which considers only standard spherical ion approximations. $E_f = -D(<0)$.

In SbO_3E tetrahedrons, the highest energy is observed not for the shortest but for the longest bond SbO_1.

Table VIII gives the various terms of the

TABLE VII

LATTICE ENERGY AND IONIC CHARACTER

$$\sum_{ij} (I_i + A_j) = (E_f - E_r) = (\lvert E_r \rvert - D)$$

	MnSb$_2$O$_4$	NiSb$_2$O$_4$	ZnSb$_2$O$_4$	FeSb$_2$O$_4$
$D = -E_f$ (kcal/mole)	762.8	797.8	747.4	792.2
$-E_r$ (kcal/mole)	1085	1055	1068	1080
$\lvert E_r \rvert - D$ (kcal/mole)	322	257	321	288
$(I_i + A_j)^a$ (kcal/mole)	3612	3676	3710	3635
$(I_i + A_j)^b$ (kcal/mole)	462	524	560	484

^{a} Calculation for standard state: $Me^{2+}(Sb^{3+})_2(O^{-2})_4$.
^{b} Calculation for standard state: $Me^{2+}(Sb^0)_2(O^{-1})_2(O^0)_2$.

bond energies: A is related to repulsion; m is considered as constant for each cation Me; B is related to coulombian attraction; r_{calc} is the calculated value obtained after having fixed the value m at a mean value for each kind of cation (Me^{II} or Sb^{III}); r_{obs} is the experimental value used to eliminate A in the relations used to derive $U(r)$.

In the case of Sb–O bonds, the value $m = 9$ has been chosen as an average indicating that the action of repulsive potential is at distances shorter than for Me–O bonds: in this later case, the value $m = 7$ indicates a repulsive action of potential at longer distances which is consistent with the weak density of the electron heart of these Me atoms. In other terms, when considering compression effects, this means that Sb^{III} electron core is "hard" while that of Me^{II} atoms is "soft."

The A values show quasi "isotropic" repulsion component for MeO bonds in octahedrons while the corresponding values for Sb–O bonds in SbO_3E tetrahedrons seem to reveal some anisotropic behavior due to the presence of the lone pair E. In other terms the Sb^{III} electron core should not be spherical because of the free hybrid orbital occupied by an electron pair ($5s^25p^3 \rightarrow 4 \times (sp^3)$ hydrids).

The B values seem to be strongly sensitive to atomic sites of O_1 and O_2 atoms and especially to space orientation of related

TABLE VIII

POTENTIAL PARAMETERS FOR MnSb$_2$O$_4$

	Mn–O$_1$	Mn–O$_2$	Sb–O$_1$	Sb–O$_2$
$-U(r)$ (kcal/mole)	52.60	65.20	128.70	102.50
A^a (10^{-90})	1533.87	1494.49	1470.31	948.01
B^a (10^{-30})	92.16	112.89	202.75	156.67
$r_{calc.}$ (Å)^b	2.2099	2.1273	1.92	1.87
$r_{obs.}$	2.214	2.132	2.01	1.95

Note. Because of uncertainties on $\bar{d}$ values, $r_{calc.}$ and $r_{obs.}$ are not similar in the case of Sb–O bonds but the inequality $r(SbO_1) > r(SbO_2)$ is well simulated.
^{a} A in IU; B in IU.
^{b} r is calculated from $(r)_{calc} = (mA/nB)^{1/m-n}$ with m fixed at a mean value; Me–O, $m = 7$; Sb–O, $m = 9$.

bonds: MeO_1 and SbO_2 bonds are lying in the same (a,b) plane while MeO_2 and SbO_1 bonds are inclined bonds (see Fig. 1). As a consequence, the Madelung contributions (β in the present model) due to ionic interactions of atomic environment are quite different when localization and space orientation of bonds are different in these MeX_2O_4 structures; it should result in different B values (Table VIII):

$$B(MeO_1) < B(MeO_2)$$

$$B(SbO_2) < B(SbO_1).$$

Thus, two complementary features (presence of lone pair and site symmetries) should condition the anomalous behavior observed for Sb–O bonds:

$$|U(Sb - O_1)| > |U(Sb - O_2)|$$
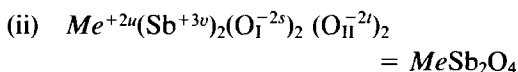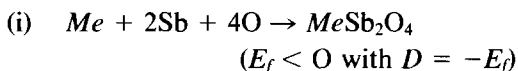
and

$$r(SbO_1) > r(Sb - O_2).$$

Let us recall that such a behavior is coherent with the various "experimental" values A, B, and m which result from electron distributions, existence of lone pair, and anisotropic environments (Madelung contributions for each bond).
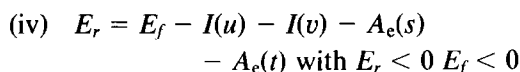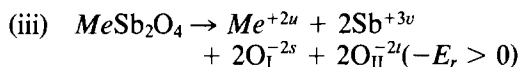
V.2. The Lattice Energy E_r

In this section we try to define the exact sense of the E_r energies calculated above.

The E_r quantity is related to the classical dissociation energy D ($D > 0$) through the ionization energies of cations I_i ($I_i > 0$) and through the electron affinities A_e of anions (oxygen).

One can use the following chemical equations:

(i) $Me + 2Sb + 4O \rightarrow MeSb_2O_4$

$$(E_f < O \text{ with } D = -E_f)$$

(ii) $Me^{+2u}(Sb^{+3v})_2(O_I^{-2s})_2 (O_{II}^{-2t})_2$

$$= MeSb_2O_4$$

$$Me \rightarrow Me^{+2u} + 2u\bar{e} \quad (+I_{Me}(^u) > O)$$

$$Sb \rightarrow Sb^{+3v} + 3v\bar{e} \quad (+I_{Sb}(^v) > O)$$

$$O_1 + 2s\bar{e} \rightarrow O_I^{-2s} \quad (+A_e(^s) > 0 \text{ or } <0)$$

$$O_{II} + 2t\bar{e} \rightarrow O_{II}^{-2t} \quad (+A_e(^t) > 0 \text{ or } <0).$$
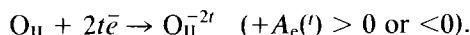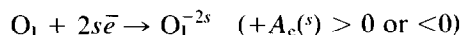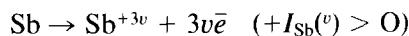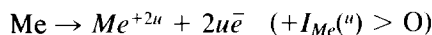
Generally I and A_e are known from literature only for pure ionic states: Me^+, Sb^+, Me^{2+}, Sb^{2+}, Sb^{3+}, O^{-1}, O^{-2}.

(iii) $MeSb_2O_4 \rightarrow Me^{+2u} + 2Sb^{+3v}$
$$+ 2O_I^{-2s} + 2O_{II}^{-2t}(-E_r > 0)$$

(iv) $E_r = E_f - I(u) - I(v) - A_e(s)$
$$- A_e(t) \text{ with } E_r < 0 \; E_f < 0$$

The electroneutrality is obeyed when

$$2u + 6v = 4s + 4t.$$

In the present case, the I_i and A_{je} terms are not known; from the determinations of E_r and D (or E_f) it is possible to deduce:

$$\Sigma_{ij}(I_i + A_{je}) = E_f - E_r = |E_r| - D.$$

Let us note that with the simple hypothesis that bonds are either ionic or covalent one can derive for $Me = Mn$ for example:

$s = 1/2$ so, $A_e(1/2) = A_e(O^{-1})$
$$= -1.45 \text{ eV}; \; t = 0 \; A_e(O^0) = 0$$

$u = 1$ so, $I(u = 1) = I(Mn^{+2})$
$$= +7.4 + 15.6 = 23.0 \text{ eV}.$$

The electroneutrality gives $v = 0$; so, $I(0) = I(Sb^0) = 0$. As a result,

$$\Sigma(I + A_e) = 23 - 2 \times 1.45$$
$$= 20.1 \text{ eV} = 462.3 \text{ kcal mole}^{-1}.$$

As a consequence one can expect $|E_r| - D = 20.1 \text{ eV} \sim 462 \text{ kcal/mole}$, i.e., the dissociation energy should be about

$$D = 1085 - 462 = 623 \text{ kcal} \cdot \text{mole}^{-1}$$
$$\text{in the case of } MnSb_2O_4.$$

Similar quantities can be obtained for the $Me = $ Ni, Zn, Fe compounds.

V.3. The Dissociation Energy $D = \Sigma_i n_i D_i$

The dissociation energies can be evaluated from the individual bond energies ($E_f = -D$) of Table VI. They are given in Table VII for 1 mole MeSb$_2$O$_4$ at 300 K in kcal · mole^{-1}. The $|E_r|$ values are indicated for comparison in Table VII.

With regard to the various uncertainties, it is noticed that the difference $|E_r| - D$ related to the ionic character of each MeSb$_2$O$_4$ compound is about 300 kcal · mole^{-1}.

The hypothetic value obtained under section IV was 462 kcal · mole^{-1}; it has been calculated from very rough speculations. However, the orders of magnitudes are comparable. So, it can be concluded that the differences $|E_r| - D$ obtained using the two methods presented here are representative of global charge transfers in these ionocovalent compounds.

In analyzing the individual energies one can notice that the mean $|E_r|$ and D terms are respectively about 120 and 90 kcal · mole^{-1} for Sb–O bonds, thus indicating a strong covalent character for these bonds. In contrast, these energetic terms are rather different for Me–O bonds ($|E_r| - D \sim$ 60–40 = 20 kcal · mole^{-1} for one Me–O bond considered as a "mean" bond); this feature is in good agreement with our initial considerations (magnetic moment at 5 K, Raman spectroscopy): the Me–O bonds can be considered to be principally ionic, the $Me^{2+(HS)}$ state being an acceptable approximation. In addition, due to the hard sphere and constant size approximation involved in the calculation of D, it is not possible to distinguish the effective ionic character of each Sb–O bond: only mean E_i values have to be considered in the present case.

Conclusion

Using two different methods, half theoretical and half experimental, it was possible to calculate individual bond energies and to predict dissociation and lattice energies for a solid compound independently of any direct measurements. These approaches should be of the greatest interest to understanding the relationships between local and macroscopic properties.

Even if the accuracy of the present calculated bond energies have to be improved, we have been able to propose for the first time a local study of the chemical bond in oxides: each bond can be characterized by five quantities:

—the length r_0 (diffraction experiments);
—the force constant f (vibrational studies);
—the thermal expansion α (diffraction);
—the bond energy (coordination energy) E_r (model I);
—the dissociation energy $D = -E_f$ (model II).

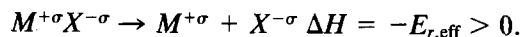In this paper, we deal in fact with three kinds of molar energies of lattice.

1. Molar classical dissociation energy corresponding to

$$M^+X^- \rightarrow M^\circ + X^\circ \quad \Delta H = -E_f > 0.$$

2. Molar classical lattice energy corresponding to

$$M^+X^- \rightarrow M^+ + X^- \quad \Delta H = -E_r > 0.$$
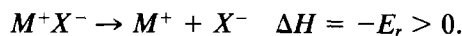
3. Molar "real" or "effective" lattice energy corresponding to

$$M^{+\sigma}X^{-\sigma} \rightarrow M^{+\sigma} + X^{-\sigma} \quad \Delta H = -E_{r,\text{eff}} > 0.$$

It results obviously in

$$E_f = E_r + \sum_{ij} (I_i + A_j)$$

$$E_f = E_{r,\text{eff}} + \sum_{ij} (p_i \cdot \Delta I_i' + I_i')$$
$$+ (q_j \cdot \Delta A_j' + A_j'),$$

where the p_i, q_j factors are directly related to the effective degree of ionicity (covalency) (they might be linearly correlated with the effective charges as a rough approximation. The I_i and A_j, I'_j and A'_j terms can be obtained from two extreme standard states.

In the case of $MnSb_2O_4$, for example, it is possible to compare the experimental $|E_r| - D$ value obtained in Table VII (322 kcal · mole^{-1}) with the calculated values corresponding to standard ionic states:

(a) $Mn^{2+}Sb^0_2(O^{-1})_2(O^0)_2$: $(|E_r| - D)_{calc}$
$$= 462 \text{ kcal} \cdot \text{mole}^{-1}$$

(b) $Mn^{2+}(Sb^{3+})_2(O^{-2})_4$: $(|E_r| - D)_{calc}$
$$= 3612 \text{ kcal} \cdot \text{mole}^{-1}.$$

This last hypothetic value was obtained using I_i and A_j values of the Me^{2+}, Sb^{3+}, O^{2-} ions (24).

Obviously, only the first ideal state (a) seems to be congruent with the experimental energetic "charge transfer" term of 322 kcal · mole^{-1}. Similar conclusions could be drawn in the case of the other isomorphous $MeSb_2O_4$ compounds (see Table VII).

Acknowledgments

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