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Thermoelastic Properties of Superoxide

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Abstract
We have applied an Extended Three Body Force Shell Model (ETSM) by incorporating the effect of translational- rotational coupling for the investigation of thermoelastic properties such as cohesive energy(, molecular force constant(*f*), compressibility(β), Restrahlen frequency ( ), Debye temperature (θ_D), Gruneisen parameter (γ), second Gruneisen parameter (q), Moelwyn Hughes constants (F_1), and ratio of volume expansion coefficient (α_v) to volume specific heat (c_v) of superoxide materials NaO_2 and KO_2 at 300K. Besides this we have calculated static shear modulii (c_{44}). The shear modulii computed between the temperatures ranges 50K to 500K. Here, we could compare our result with experimental data for thermal properties only at room temperature and the magnitudes of SOECs seem to be correct, also the ETSM method produces the sign of SOECs correctly.
Keywords: Orientationally Disordered Materials, Shear modulii, ETSM, TR coupling, Elastic constants]
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1. Introduction

Superoxide is unique among alkali-metal superoxide with chemical formula XO_2 (where X=Na, K, Rb, Cs) can be regarded as an ionic molecular crystals in which the molecular ion O_2^- [1,2] play the role of anion and exhibit a wide variety of phenomena, which can be directly related to the properties of the superoxide ions O_2^-. At room temperature the crystal has an orientationally disordered cubic structure (Fm3m) in which the molecular anions are undergoing rotational diffusion. The space group of low temperature phase implies that O_2^- [3] ions are still disordered with respect to head and tail. The special interest in NaO_2 lies in the fact that this exhibits the NaCl structure. The lattice constant for NaO_2 is very similar to those of NaCl and the mass of the Cl is only about 10% heavier than that of O_2^- [3]. We have applied this ETSM for the investigation of cohesive and thermal properties of Orientationally Disordered sodium superoxide which has been successful in describing the cohesive, thermal and dynamic properties of Orientationally Disordered alkali cyanides [4-6].
The Extended Three Body Force Shell Model (ETSM) is given in the next section. The result and discussion are given in the successive section.

2. Extended Three Body Force Shell Model(ETSM)

The interaction potential used to derive the framework of the present ETSM can be expressed as

$$\phi = -\frac{e^2}{2}\sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1}\left[1+\sum_{kk'} f_k(r_{kk'})\right] - \sum_{kk'} c_{kk'} r_{kk'}^{-6} - \sum_{kk'} d_{kk'} r_{kk'}^{-8} - b\sum_{kk'}\beta_{kk'}\exp\left\{\frac{r_k + r_{k'} - r_{kk'}}{\rho}\right\} + \phi^{TR} \quad (1)$$

Here k, k′ denotes the positive and negative ions respectively and sum is taken over all the ions. In the above expression, the first two terms represent the long-range coulomb and three-body interaction (TBI) [4]. The third and fourth terms are vdW coefficients due to dipole-dipole and dipole-quadrupole (d-q) interactions with $c_{kk'}$ and $d_{kk'}$ as the corresponding vdw coefficient respectively. The fifth term is Hafemeister and Flygare (HF) type [7] short-range (SR) overlap repulsion extended operative upto the second neighbour (nn) ion with $\beta_{kk'}$ as Pauling coefficient. Φ^{TR} is the contribution due to translational-rotational (TR) coupling effects [8,9]. The range and hardness (b and parameters determined from the equilibrium condition

$$[d\phi(r)/dr]_{r=ro} = 0 \quad (2)$$

where r is the nearest interionic sepration and r_o is the equilibrium separation and the bulk modulus,

$$B=(9kr_o)^{-1}[d^2\phi(r)/dr^2]_{r=ro} \quad (3)$$

With K as the crystal structure constant (K=2 for NaCl structure).
Using the equ.(1) and the straight forward method the shear elastic constant c_{44} is calculated as follows

$$c_{44} = -2.0666T\beta B_T + \frac{e^2}{4r^4}\left[\frac{A_1}{6} - 1.3666B_1 + \frac{A_2}{2} - 1.5333B_2\right] + \delta c_{44}^{TR} + \delta c_{44}^{an} \quad (4)$$

We have calculated the cohesive, thermal and elastic properties, using the expression given in our earlier paper [10-11]

3. Result and Discussion:

Using the input data of ref [12-14] given in Table 1, we have computed the model parameter b,ρ and f(r) listed in Table 2 in the ETSM framework.

Table 1 Input data for NaO_2 and KO_2 at room temperature.

Compound	**NaO_2**	**KO_2**
Properties	Values	Values
r_0 (Å)	2.75	3.08
c_{11} (10^{11}dyn cm^{-2})	5.80	4.99
c_{12} (10^{11}dyn cm^{-2})	4.50	4.29
c_{44} (10^{11}dyn cm^{-2})	3.80	4.09
α_+(Å)^3	0.28	1.30
α_- (Å)^3	2.45	2.45

Table 2. Model Parameters for NaO_2 and KO_2 at room temperature.

T(K)	r_0(Å)	Å	b(10^{-12}erg)	f(10^{-2})
300**(NaO_2)**	2.748	0.204	0.759	-0.0055
300**(KO_2)**	3.104	0.1835	0.6370	-0.0020

On taking the model parameters we have calculated the cohesive energy ( ), molecular force constant (f), compressibility (β), Reststrahlen frequency(,Debye temperature (θ_D), Gruneisen parameter (γ), second Gruneisen parameter (q), Moelwyn Hughes constants (F_1), and ratio of volume expansion coefficient ( ) to volume specific heat (c_v) at room temperature listed in Table 3. The results on all these properties are in good agreement with the experimental data available at room temperature. Finally the ETSM seems to be realistic model. for explaining cohesive and thermal properties of Orientationally Disordered Materials

Table 3. Cohesive and thermal properties of NaO_2 and KO_2

Properties	**300K(NaO_2)**	**300K(KO_2)**
kJ/mol^{-1})	-830.78**(799[a])**	-741.57(741[a])
f(10^4dyn.cm^{-1})	2.9277**(3.345[c])**	2.203
dyn.cm^{-1})	5.630**(4.933[b])**	8.453
$_o$(THz)	5.787	5.020
Θ_D(K)	277.76	240.94
$_V$ c_V(10^3J)	4.077	4.152
	2.593	3.239
q	2.620	3.291
F_1	6.371	7.229

a-[15]; b-[values calculated from $c_{11}+2c_{12}/3$]; c-[obtained from $=3kr_0/f$]

Besides this we have calculated the shear modulii computed between the temperatures ranges 50K to 500K as shown in figure 1. The magnitudes of SOECs seem to be correct, also the ETSM method produces the sign of SOECs correctly. Our result on these properties is in good agreement with the experimental data available only at room temperature.

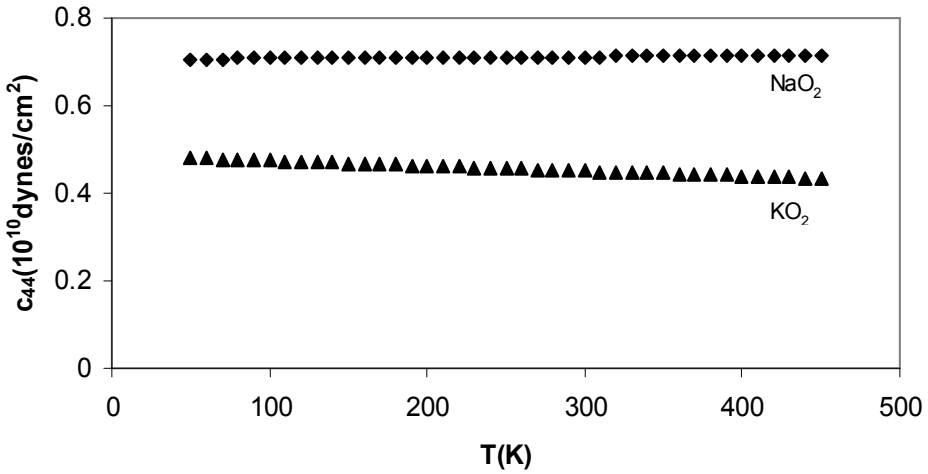

Figure 1. Second Order Elastic Constant c_{44} as a function of temperature; square (■) and triangle (▲) represents the c_{ij} for NaO_2 and KO2 respectively.

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