Calculated polarization and piezoelectric constants of $NaNO_2$†

Kam-shing Kam and John H. Henkel

Department of Physics and Astronomy, The University of Georgia, Athens, Georgia 30602

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The electronic energy band structure of ferroelectric sodium nitrate has been calculated using an $X\alpha$ exchange and a plane-wave Gaussian basis set. Three piezoelectric-strain constants (d_{21}, d_{22}, d_{23}) also have been calculated by assuming that the boundaries of a molecule in a crystal are given by minimum charge-density surfaces and that the displacements of atoms in the strained crystal are directly proportional to the strains. The calculated values of d_{21}, d_{22}, and d_{23} in units of 10^{-8} esu/dyn range from $d_{21}=-7.69$, $d_{22}=6.26$, and $d_{23}=-3.23$ to $d_{21}=-9.09$, $d_{22}=6.75$, and $d_{23}=-3.69$ depending upon the choice of elastic-stiffness constants. These values compare favorably with the only experimental values measured by Hamano *et al.*, which are $d_{21}=-8.5$, $d_{22}=5.0$, and $d_{23}=-3.5$.

I. INTRODUCTION

Since the discovery of ferroelectricity in $NaNO_2$ by Sawada and co-workers,[1] various properties of $NaNO_2$, such as thermal, dielectric, optical, elastic, phase transition, electric conductivity and susceptibility, and ir and Raman spectra have been extensively studied by many researchers.[2–9] Refined structural analysis has been made by Carpenter,[10] Truter,[11] and Kay and Frazer[12] since Ziegler's first structural determination of $NaNO_2$ in 1931.[13] It was found[2] that $NaNO_2$ undergoes a first-order phase transition from ferroelectric to the sinusoidal antiferroelectric phase at the Curie point ($T_c=163.9$ °C), which is followed by a second-order phase transition to the paraelectric phase at the Neél temperature ($T_N=165.2$ °C). In the paraelectric phase, $NaNO_2$ has a nonpolar orthorhombic structure with a D_{2h}^{25} ($Immm$) space group and is not piezoelectric. In the ferroelectric phase, with its polarization axis along the b axis, it has a polar body-centered orthorhombic structure with a C_{2v}^{20} ($Im2m$) space group and it is piezoelectric.

Although sodium nitrite has been under study for more than 40 years, there has been very little work done on the piezoelectric constants[14] and on the overall electronic band structure[15] of the crystal. In this paper, we present (i) the electronic band structure for ferroelectric $NaNO_2$ calculated using an $X\alpha$ exchange and a mixed plane-wave Gaussian basis set,[16] and (ii) a method for calculating three piezoelectric-strain constants d_{21}, d_{22}, d_{23} for ferroelectric $NaNO_2$.

II. BAND STRUCTURE OF FERROELECTRIC $NaNO_2$

The orthorhombic unit cell of $NaNO_2$ crystal in the ferroelectric phase is shown in Fig. 1 with Carpenter's values of the lattice parameters and the atomic positions appearing in the caption. The corresponding Brillouin zone is shown in Fig. 2, where the symmetry points and lines are labeled.

The energy bands for ferroelectric $NaNO_2$ have been calculated using a mixed basis of plane waves and Gaussian and using an $X\alpha$ exchange. The value of the exchange constant for $NaNO_2$ used was 0.74 which is the average value of Schwartz's[17] virial theorem values of Na, N, and O. Crystalline Bloch wave functions were calculated for the Γ, R, S, T, and X symmetry points in the first Brillouin zone with the electronic charge density averaged over these five

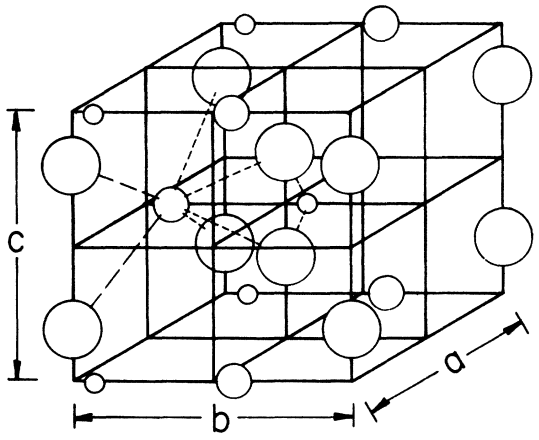

FIG. 1. Orthorhombic unit cell of the ferroelectric $NaNO_2$. Large, medium, and small circles represent oxygen, sodium, and nitrogen, respectively. $a=3.55$ Å, $b=5.56$ Å, $c=5.38$ Å, $Y(\mathrm{Na})=0.5862b$, $Y(\mathrm{N})=0.1188b$, and $Z(\mathrm{O})=0.1944c$.

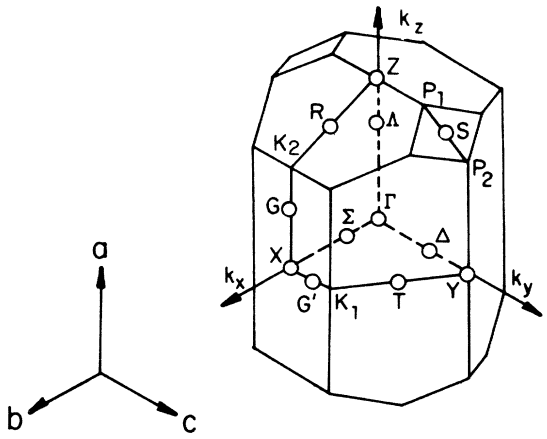

FIG. 2. Brillouin zone of the ferroelectric $NaNO_2$.

points with weights 1, 2, 2, 2, 1. Convergence of the eigenvalues was obtained to within 0.05 eV.

The resulting band structure for ferroelectric $NaNO_2$ is shown in Figs. 3, 4, and 5. The band gap at Γ is 3.45 eV; the indirect band gap is about 2 eV and the interband gap is between 2.7 and 6.3 eV. These values agree reasonably with the experimental resistivity gaps of 2.4,[18] 2.6, 3.1, 2.3, and 3.7 eV for different current directions[7] and with absorption peaks of 3.14 (Ref. 19) and 3.22 eV.[20]

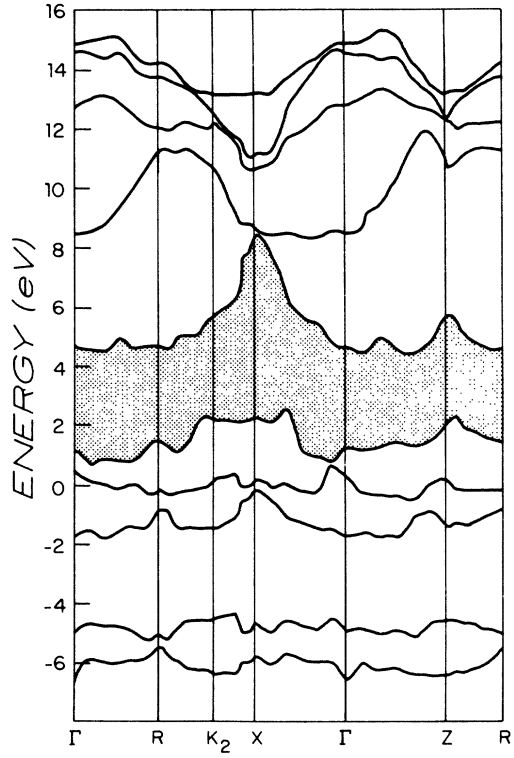

FIG. 4. Energy band structure for the ferroelectric $NaNO_2$.

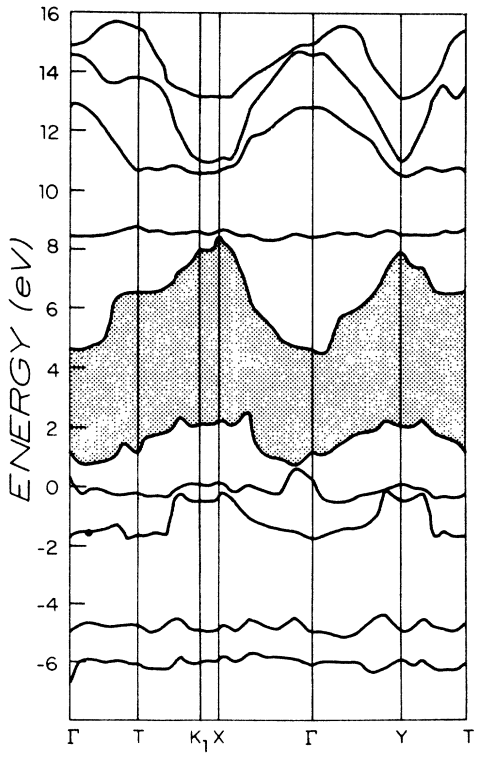

FIG. 3. Energy band structure for the ferroelectric $NaNO_2$.

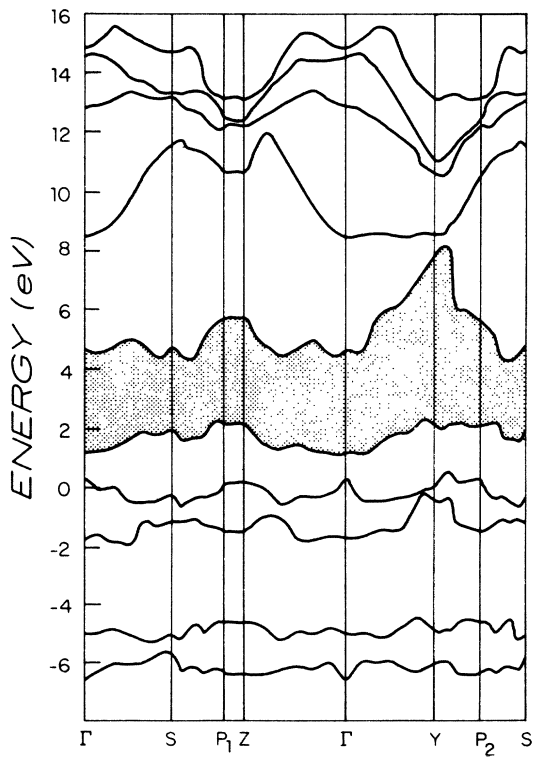

FIG. 5. Energy band structure for the ferroelectric $NaNO_2$.

III. PIEZOELECTRIC CONSTANTS

A. General

According to convention,[21] for any piezoelectric crystal, the change in polarization ΔP_l produced to the lowest order in the strains S_j can be written

$$\Delta P_l = e_{lj} S_j + \epsilon^{s}_{lm} E_m = d_{li} c^{E}_{ij} S_j + \epsilon^{s}_{lm} E_m \quad , \tag{1}$$

where the notations have the following meanings: e_{lj} are the piezoelectric-stress constants, d_{li} are the piezoelectric-strain constants, c^{E}_{ij} are the elastic-stiffness constants at constant electric field, E_m are the external electric field components, ϵ^{s}_{lm} are the dielectric susceptibilities at constant strains, and l,m,i,j are summing indices with $l,m=1,2,3$, $i,j=1,2,3,4,5,6$.

In the absence of the external electric field, Eq. (1) can be simplified to

$$\Delta P_l = e_{lj} S_j = d_{li} c^{E}_{ij} S_j \quad . \tag{2}$$

For a piezoelectric crystal which is also ferroelectric, Eq. (2) can be further expressed as

$$P^{n}_{l} - P^{0}_{l} = e_{lj} S^{n}_{j} = d_{li} c^{E}_{ij} S^{n}_{j} \quad , \tag{3}$$

where P^{0}_{l} is the spontaneous polarization without any strains and fields and P^{n}_{l} is the component of the total polarization in the l direction due to the presence of the nth set of strains S^{n}_{j}.

The values of the piezoelectric-stress constants e_{lj} can be calculated from Eq. (3) once P^{0}_{l} is known and P^{n}_{l} calculated for several sets of strains S^{n}_{j} while the values of the piezoelectric-strain constants can then be calculated if c^{E}_{ij} are known.

B. Piezoelectric-strain constants d_{21}, d_{22}, and d_{23} of $NaNO_2$

To evaluate d_{21}, d_{22}, and d_{23} for ferroelectric $NaNO_2$ with its ferroelectric axis along the b axis, we need to calculate P^{0}_{2} and P^{n}_{2} (for $n=1,2,3$), where the nonzero strain components have been chosen to be (i) for $n=1$, $S^{1}_{1}=0.003$; (ii) for $n=2$, $S^{2}_{2}=-0.0025$; and (iii) for $n=3$, $S^{3}_{3}=0.003$. By assuming that the relative cell positions of atoms in $NaNO_2$ are unchanged under small strains, the energy bands for $NaNO_2$ under each strain are calculated in the same manner as done in Sec. II for the unstrained $NaNO_2$ except the convergence of the eigenvalues were obtained to only 0.3 eV due to lack of computer time. The polarizations P^{n}_{2} (for $n=0,1,2,3$) are then calculated using the assumption that the boundaries of a neutral molecule are represented by minimum surface contours[22] of the electronic charge densities obtained from the fifth iterated band calculation. As a result, the calculated values of the three piezoelectric-stress constants e_{21}, e_{22}, and e_{23} in units of esu/cm^2 are $-22\,798.30$, $-21\,169.85$, and $-25\,540.95$.

TABLE I. Experimental and calculated values of the three piezoelectric-strain constants d_{21}, d_{22}, and d_{23}. Columns (1), (2), and (3) correspond to the calculation using Shimizu, Hauret, and Ota's values of the elastic-stiffness constants.

	Experimental values (Ref. 14)	Calculated values (this paper) (1)	(2)	(3)
d_{21}	−8.5	−7.67	−8.33	−9.09
d_{22}	5.0	6.26	6.75	6.55
d_{23}	−3.5	−3.23	−3.69	−3.53

With the calculated values of e_{21}, e_{22}, and e_{23} and the experimental values of the elastic stiffness constants determined by several researchers,[5,23,24] the values of the three piezoelectric-strain constants of ferroelectric $NaNO_2$ at zero external electric field can be determined[25] from Eq. (3). The calculated and the experimental values of d_{21}, d_{22}, and d_{23} of ferroelectric $NaNO_2$ in units of 10^{-8} esu/dyn are shown in Table I.

The calculated values of d_{21} and d_{23} agree with the experimental values to within 10%, while the calculated value of d_{22} is about 35% larger than that of the experimental value. If more iterations had been made to obtain better convergence of the energy bands, the calculated value of the piezoelectric-strain constants would have been in better agreement with experiment as the calculated value of d_{22} was converging towards the experimental value.

IV. SUMMARY

The energy band structure and three piezoelectric constants for ferroelectric $NaNO_2$ have been calculated. The reasonable agreement between the calculated and the experimental values of the three piezoelectric constants suggests that the assumptions used in the present calculation can be used to calculate polarization and piezoelectric constants for other ferroelectric and piezoelectric crystals.

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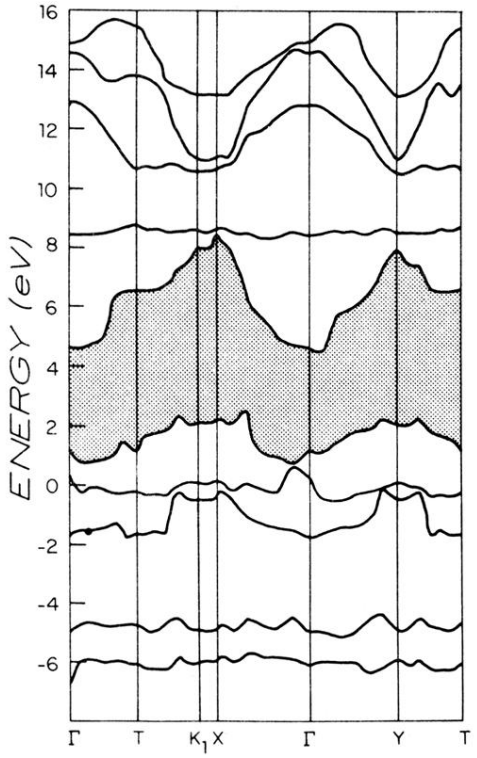
[25]It is assumed that stiffness constants at constant electric field E are equal to the stiffness constant at constant electric displacement D.



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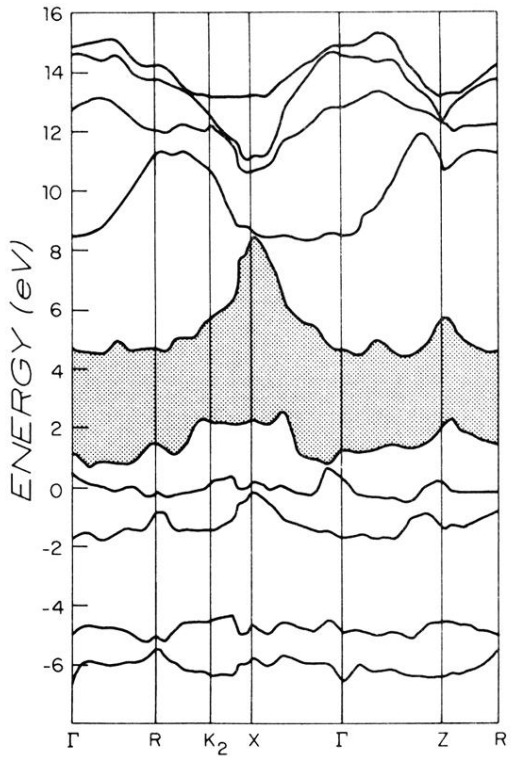

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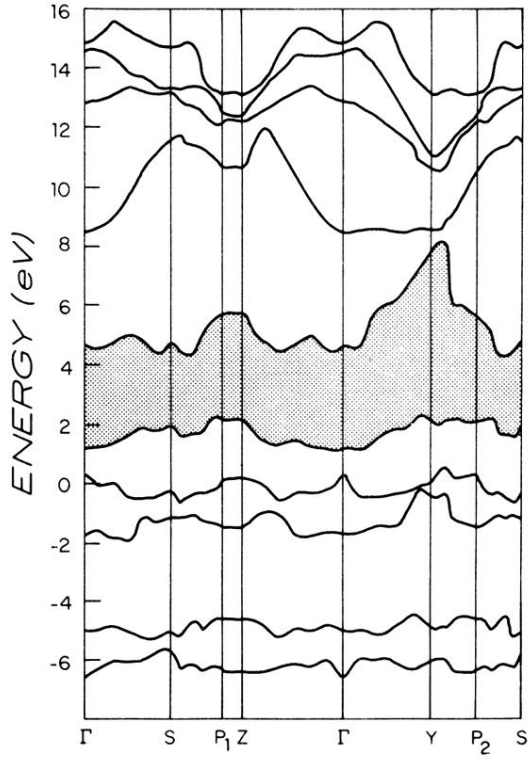

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