BAND STRUCTURE OF SOME SOLIDS

THESIS

Submitted for the Ph. D. Degree
in Physics

Presented by

HATEM FAHIM HASSAN

B. Sc. & M. Sc. in Physics

PHYSICS DEPARTMENT
FACULTY OF SCIENCE
AIN SHAMS UNIVERSITY

1983

بسم الله الرحمن الرحيم

" تبارك الذى بيده الملك وهو على كل شيئ قدير ه الذى خلق الموت والحياه
ليبلوكم ايكم احسن عملا وهو العزيز الغفور ه الذى خلق سبع سماوات طباقا
ما ترى فى خلق الرحمن من تفاوت فارجع البصر هل ترى من فطور
ثم ارجع البصر كرتين ينقلب اليك البصر خاسئا وهو حسير " .

سورة الملك

بسم الله الرحمن الرحيم

ACKNOWLEDGEMENT

I would like very much to express my feeling of deep gratitude to Prof. Dr. Abd-El-Aziz Aly Mohamed, Chairman of Physics Department, Faculty of Science, Ain Shams University, for his sincere help and eminent supervision.

Cordial thanks are also due to Dr. Abd-El-Fattah Mohamed El-Dib, Assistant Professor at Physics Department, Faculty of Science, Al-Azhar University, for his sincere and kind help, invaluable guidance, encouragement and eminent supervision.

CONTENTS

ABSTRACT

This work deals with the study of the electronic band structure of sodium nitrite crystal $NaNO_2$. The band structure has been studied at different temperatures. In addition, the temperature dependence of the energy gap, electron velocity and effective mass have been also calculated. The concept of zero-approximation was applied to obtain the temperature dependence of the atomic charges as well as the temperature dependence of spontaneous polarization of sodium nitrite crystal. The values of the spontaneous polarization at different temperatures have been used to calculate the piezoelectric-strain constants in the absence of an external electric field.

The calculations are carried out using a semi-empirical method within the frame of the linear combination of the atomic orbitals method (LCAO). Two equations for determining the Hamiltonian matrix elements have been introduced to be applicable for the calculations of the band structure of crystals in the direct and reciprocal spaces. A similar treatment is also given for the overlap matrix elements. When it is needed a self-consistent charge procedure is supplied to the method.

The results show that the charges on atoms and the spontaneous polarization (P_s) depend slightly on temperature. The piezoelectric-strain constants which have been calculated using the values of P_s at different temperatures show good agreement with experimental values.

The analysis of the wave functions indicates that the NO_2^- group in the $NaNO_2$ crystal forms a rigid complex, the energy levels of which are approximately repeated with the same values in the zero approximation and at Γ-point of the crystal (without considering the Madelung potential). The study of the electronic wave functions at different points in the Brillouin zone shows that the electronic wave functions of the filled bands depend slighly on the wave vector $\underline{k}$. It is shown also that the electronic wave functions of the filled bands are approximately the same as those obtained at Γ-point. For this reason, the results of the zero-approximation give a good results for the effective charges and spontaneous polarization of the crystal.

The results show also that the electronic energy bands in sodium nitrite crystal depend slightly on temperature. The phase transition causes only an energy shift for the electronic energy bands. The points in the Brillouin zone at which the minimum energy gap occurs are approximately not affected by the phase transition. The temperature dependence of the energy gap shows that the change in the width of the forbidden energy gap (Eg) due to phase transition is about -0.23 eV, and that Eg changes linearly with temperature in each phase with different coefficients. The value of the energy gap obtained in this work at 20°C is 3.27 eV which is in good agreement with the experimental value (3.14 eV) obtained at the same temperature.

The temperature dependence of the effective mass m^* shows that, at the point of minimum energy gap, $|m^*_{zz}|$ increases smoothly as the temperature approaches the phase transition region. It is also observed that the value of m^*_{zz} increases and decreases sharply and irregularly with temperature within the region of phase transition. Also, it is shown that the effective mass m^*_{zz} has irregular dependence on the wave vector $\underline{k}$ as the temperature approaches the phase transition region. At 160°C, m^*_{zz} shows some oscillations with k_z. This irregular k-dependence disappears gradually as we go far from the phase transition region. From the analysis of the temperature dependence of the electron velocity and the effective mass in different directions, one can predict that the mobility differs from one direction to another, while it depends slightly on temperature. From the analysis of the **results of the effective mass,** it is expected that an exciton level near the valence band may be formed. This will reduce the electric conductivity of the crystal.

INTRODUCTION

Material Used

1. Crystal Structure and Phase Transition

Sodium nitrite, $NaNO_2$, has excited extensive investigation since the discovery of its phase transition by Sawada et al(1). At room temperature, the Bravais Lattice of $NaNO_2$ is determined by X-ray(2) and neutron diffraction studies(3). It has a body centered orthorhombic Im2m-C_{2v}^{20} space group with one formula unit per primitive cell. The spontaneous polarization (parallel to the b-axis) has two contributors. The frist one is the unit-cell dipole moment established by the position of the Na^+ cation and NO_2^- anion in the crystal lattice. The second is the intrinsic dipole moment of the NO_2^- anion which are aligned in the bc-plane in such a way that their electric dipole moments are all pointing parallel to the b-axis (Fig. (I.1)).

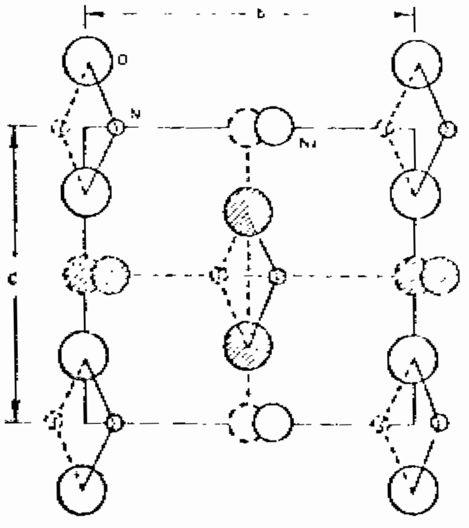

Fig. (I.1): Unit cells of $NaNO_2$.

The atoms shown with the solid circles represent atomic positions in the ferroelectric phase (C_{2v}^{20}). The dashed circles correspond to the paraelectric phase (D_{2h}^{25}). (Dimensional changes of the unit cell have been omitted). The shaded atoms are in the plane ½ of a lattice spacing in the a direction.

This simple ferroelectric ordered phase is separated from the disordered paraelectric phase by a sinusoidal antiferroelectric phase which is stable over only a very narrow temperature range of order 1.5°K. At $T = T_c \approx 163^{\circ}C$ a first-order transition takes place to an antiferroelectric phase in which the average dipole moment along the b-axis for any plane of nitrite ions normal to the a-axis, display a sinusoidal modulation along the a-axis(4,5). This sinusoidal ordering has a period of about 8a, although the precise period may decrease slightly with increasing temperature. However, by increasing the temperature a second-order transition at $T_N \approx 164.5^{\circ}C$ takes place at which the system becomes paraelectric with space group Immm-D_{2h}^{25}.

Kay(3) used an accurate neutron diffraction method to define the mechanism of transition. It was shown that the phase transition inserts a mirror plane perpendicular to the b-axis. The nitrite and sodium ions are disordered on either, but not both, sides of this plane in any one primitive cell. The nitrite ion can now point in either direction along the b-axis and the sodium ion has centered itself on the unit-cell edge parallel to the b-axis (Fig. (I.1)). However, the Raman spectroscopy investigation of the paraelectric phase of $NaNO_2$ crystal(6) shows more resonance than allowed group theoretically by the D_{2h}^{25} space group symmetry. This is simply an illustration of the fact that the higher symmetry of the paraelectric phase is only of statistical nature with a flipping time of the nitrite ion which is long compared with the period of the optical phonon frequency.

The point of contention is the manner in which the nitrite ion moves between its two configurations. Since the internal O-N-O bending frequency remains high throughout, a motion confined to the bc-plane is ruled out. There are in fact numerous claims in the literature of evidence in favour of flipping about either the a-axis or the c-axis(3,7). It is, of course, not impossible that both mechanisms could be playing a significant role.

Recently, Ivanova and Chisler(8) have investigated the infrared spectroscopy of the ferroelectric transition of the $NaNO_2$ crystal. It was shown that new absorption bands appear on approach to the ferroelectric transition temperature $\sim 163^{\circ}C$. These bands were attributed to the hindered rotation of the NO_2^- groups about their a-and c-axes. The integrated intensities of these bands were used in a calculation of the potential barriers H_a and H_c hindering the rotation of the NO_2 group about the a- and c-axes. Figs. (I.2) and (I.3) show the dependence of these barriers on the temperature. Between 160°C and 185°C the dependence of H_a and H_c had a plateau which indicated the existence of an intermediate phase. It was also concluded that the main process which destroyed the ferroelectric state is the rotation of the NO_2 radical about the a-axis.

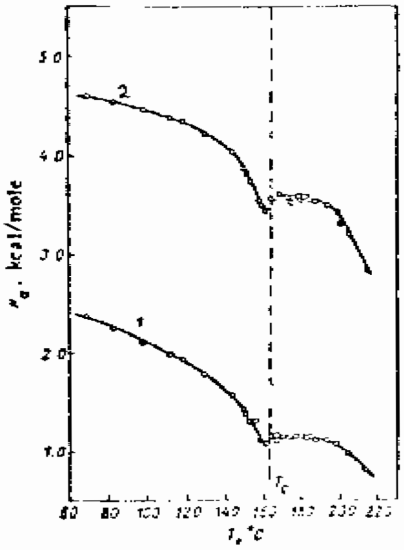

Fig.(I.2): Potential barrier H_a hindering the reorientation of the NO_2^- radical about the a-axis, perpendicular to the radical plane. 1) Calculations based on classical statistics, and 2) Calculations based on a quantum model.

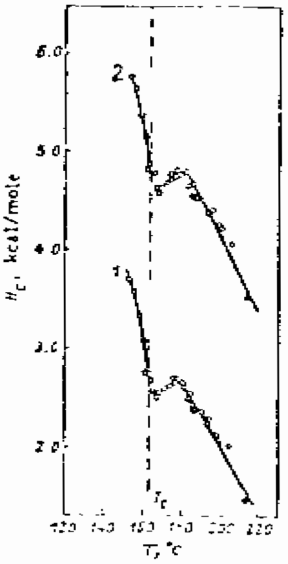

Fig.(1.3): Potential barrier H_c hindering the orientation of the radical NO_2^- about the c-axis, parallel to the O-O bond. Curves 1 and 2 have the same meaning as in Fig. (I.2).

According to the structure determination of $NaNO_2$ crystal given by Kay et al., the unit cell dimensions in the ferroelectric phase[9] at temperature 20°C are:

$a = 3.56$, $b = 5.563$ and $c = 5.384$ A°

while the bond lengths are:

Na-N = 2.589 , Na-O = 2.471 and N-O = 1.24 A° and O-N-O angle = 114.9°.

The unit cell dimensions in the paraelectric phase(10) at temperature 185°C are:

a = 3.681 , b = 5.692 and c = 5.395 A°

while the bond lengths are:

Na-N = 2.662 , Na-O = 2.523 and N-O = 1.223 A° and O-N-O angle = 116.5°.

The atomic coordinates in the two phases are summarized in Table (I.1)(9):

Table (I.1): The atomic coordinates of $NaNO_2$ crystal in the ferro- and para-electric phases.

	Ferroelectric			Paraelectric		
	x	y	z	x	y	z
Na	0.0	0.5853	0.0000	0.0	0.5401	0.0000
N	0.0	0.1200	0.0000	0.0	0.0725	0.0000
O	0.0	0.0000	0.1941	0.0	-0.0416	0.1920
O	0.0	0.0000	-0.1941	0.0	-0.0416	-0.1920

The unit cell dimensions of the crystal at different temperature were measured by Kucharczyk(11). The results are shown in Table (I.2).