氏　　名	S. M. HASANUZZAMAN
学位（専攻分野）	博士(学術)
学 位 記 番 号	総研大甲第372号
学位授与の日付	平成１１年３月２４日
学位授与の要件	数物科学研究科　放射光科学専攻 学位規則第４条第１項該当
学 位 論 文 題 目	Electronic and Optical Properties of Three Dimensional Charge Density Wave System in $BaBiO_3$
論 文 審 査 委 員	主　査　教　授　安藤 正海 教　授　大隅 一政 助 教 授　那須 奎一郎 助 教 授　河田 洋 助 教 授　古坂 道弘 教　授　宮原　恒昱（東京都立大学） 教　授　柿崎　明人（高エネルギー加速器研究機構）

論文内容の要旨

Since the advent of high-T_c superconductivity in copper oxides by Bednorz and Müller, the interest in solid state properties of various oxides like Cu-oxide, Bi-oxide, Mn-oxide and Ti-oxides has been renewed. In these materials the noble property said to comes from the strong inter-electron correlation or the electron lattice coupling. Among those materials $BaBiO_3$(BBO) and it's related compounds $BaPb_{1-x}Bi_xO_3$(BPBO) and $Ba_{1-x}K_xBiO_3$(BKBO) are the objects of a special interest. $BaBiO_3$ becomes a superconductor if doped with Pb at the Bi sites (with a maximum of T_c ~ 12K for x ~ 0.25), and also shows superconductivity if it is doped with K at the Ba sites (with a maximum of T_c~ 30K for x ~ 0.40). In these materials electron-phonon(el-ph) coupling is inferred to play very important role, and we will focus on this el-ph coupling. It can give two properties, one is superconductivity and other is charge density wave(CDW) type insulator. Very strong el-ph coupling will give two instabilities. If it is remain in the metallic state, it will give high-T_c superconductor. But it often causes another instability like CDW state. So, these two basic possibilities come from el-ph coupling. In order to clarify strong el-ph coupling, which gives CDW, it is necessary to understand how electron couples with phonon, and how it effects on the ground state as well as excited state.

In spite of this renewed interest, the basic electronic structure of the parent material $BaBiO_3$ is still not clarified sufficiently. These materials present several peculiarities with comparing to other perovskite type high-T_c superconductor compounds. It is a three dimensional system, does not contain any magnetic ions and absence of two dimensional metal-oxygen plane. In the undoped phase of this material, a static charge density wave state with a periodic lattice distortion appears, opens up a gap at the Fermi level, and makes this compound a Peierls insulator. Furthermore, the superconductivity appears when this CDW order is destroyed by doping.

It is well known that, there are two types of gap exists in this CDW type insulator $BaBiO_3$, one is direct and another is indirect. In usual insulators, however the opening of optical gap (direct gap) and the appearances of indirect gap are often consider separately. The optical gap usually comes from the difference between the occupied and unoccupied atomic orbitals relevant to the valence and the conduction bands. While the indirect transition usually appears because of the weak electron phonon coupling, which slightly mixes up direct and indirect transitions.

On the other hand, BBO is not an ordinary insulator, a strong electron-phonon interaction is acting in this material, causes a Peierls distortion of the lattice, doubling the unit cell, opening up a wide direct gap, and makes the indirect transitions to appear. So both the direct gap and the appearance of the indirect transition have the same origin. For this reason, in our theory, we did not used the conventional perturbation approach, instead, we have developed a unified theory based on the extended Peierls-Hubbard model.

We have thus theoretically studied the electronic and optical properties of $BaBiO_3$, as one of the typical material with three dimensional CDW state, in connection with nonlinear excitations. The ground and excited states of a three dimensional extended Peierls-Hubbard models with half-filled band electrons have been evaluated. Within this model, we introduce the adiabatic approximation for

phonons, and the Hartree-Fock approximation for inter-electron coulombic interactions. The electron-hole correlation on the Bi atoms and the classical fluctuations of the oxygen sub-lattice coordinates are also taken into account, so as to obtain exciton effect as well as thermal fluctuations of the lattice.

By using our model, we at first clarified the near infrared and visible absorption spectra of BBO from a unified point of view. The direct transition corresponds to the excitation across the direct CDW gap ($\approx$ 2.0eV), and this gap arises due to the frozen part of the Peierls distortion. While the indirect part corresponds to the long tail in the infrared region of the absorption spectrum, and it is due to the excitation across the indirect CDW gap ($\approx$ 0.55eV). It arises due to the lattice fluctuations from the static Peierls distortion. This lattice fluctuation destroys the k-selection rule, and makes the indirect transition possible. Our conclusion is that, the origins of both the direct gap and indirect transitions are the same, i.e., the strong coupling between the electron and the breathing motion of the oxygen atom. These theoretical results shown good agreement with recent optical experiments on BBO.

Next, we have studied the nonlinear lattice relaxation process of exciton, and explained the origin of the photoinduced absorption in $BaBiO_3$. The adiabatic potential energy surfaces that describe the nonlinear relaxation from the Franck-Condon state to the self-trapped exciton (STE) state have been calculated within our unified theory. When the CT excitation is created by its threshold energy, the exciton is relax to a STE, and localized within the CDW gap. This localized self-trapped state partially canceled the charge density distribution of the uniform CDW ground state, and is return back towards the metallic state. It will gives a new absorption band with an energy of about a half of the energy gap ($\approx$ 0.9eV). This energy level could be observed in the photoinduced absorption measurement. The experimentally observed photoinduced reflectivity peaks at around mid-gap energy is assigned for the optical excitation from this localized state (STE) to the peak of the density of states of the conduction band.

Finally, let us briefly discuss these nonlinear excitations from a somewhat different point of view. The collective excited states described in this work can never be created by ordinary thermal excitation from the ground state, because a much larger energy is required than the ordinary thermal energy such as at room temperature. It becomes possible only when the energy is supplied by photoexcitation. That is, as a combination of the photoexcitation and the subsequent lattice relaxations, we can clarify the multistable nature of the ground state, even when thermal excitation can never access it.

論文の審査結果の要旨

Sheikh Mohammad Hasanuzzaman 君の博士論文内容は、BaBiO3 結晶の近赤外から可視域にわたる光物性に関する理論的研究である。

2eV のエネルギー間隙を持つ BaBiO3 結晶は、極めて強い電子格子相互作用を有する CDW 型の絶縁体である。BCS 型高温超伝導の母結晶としても大変有名である。それにも拘らず、その電子状態と強い電子・格子相互作用が、いかに電子状態に反映しているかに関しては、現在でも、明瞭には解明されていない。特に、最近の分光学的測定によれば、(1)CDW 型絶縁体であるにも拘らず、2eV のエネルギー間隙の中に、スペクトルが近赤外域までのびる何らかの状態がギャップ内に存在する。(2)2eV のエネルギー間隙に相当する光で励起すると、更に、全く別のギャップ内励起状態が誘起される等、不思議な現象が見いだされている。これらは、この物質の電子状態の特質や、強い電子・格子相互作用を直接反映していると思われるが、原因は全く不明である。

これを統一的に解釈するために、Hasanuzzaman 君は、Bi の 6s 軌道と酸素の 2p 軌道の強い混成を考慮した、三次元拡張パイエルス・ハバード・モデルをこの系に応用し、断熱近似、平均場近似、一重 CI 補正法、変分法、古典的モンテ・カルロ法等を用いて、この系の基底状態、光学的励起状態、及び、その格子緩和状態に関する理論計算を行なった。そして、上記の(1)は、間接遷移型励起子が、パイエルス変形の強い量子・熱揺らぎを通して、間隙内に現れたものであり、一方、(2)は、エネルギー間隙を越える直接遷移型励起子が、格子緩和後に、強い電子・格子相互作用を通して、間隙内に、自己束縛したものであることを、世界に先駆けて、理論的に立証した。

以上の研究は数物科学研究科放射光科学専攻の博士論文のレベルに値し、又、物性物理学への新しい提案をも含んでいる。従って、専門的にも総合的にも、極めて優秀な成績を挙げていると判断した。