JJAP Series 1
Superconducting Materials (1988) pp. 251-254

Electronic Structures in $BaPb_{1-x}Bi_xO_3$ and in La_2CuO_4

Tadao KASUYA and Katsuhiko TAKEGAHARA

Department of Physics, Tohoku University, Sendai 980, Japan

$BaPb_{1-x}Bi_xO_3$ 系の異常な振舞いを理解する為にその詳細なバンド計算がなされた。それから $BaPbO_3$ では空の s-p 反結合バンドをシフトすることにより基本的にはバンドモデルで説明され得ることが示された。一方 $BaBiO_3$ では Bi の 6 s 電子の強い相関が本質的に重要となり，それを局在電子として扱うモデルが基本的に良いこと，又その磁性は広い意味の近藤効果により抑えられることが示された。$BaPbO_3$ に Bi を加えた時の金属-非金属移転は Bi 6 s の相関効果によるものであり，高い超伝導転移温度はこれにより増強された電子フォノン相互作用によるものであろうという事が示された。一方 La_2CuO_4 系のバンド計算も種々なされ，3 d(x^2-y^2) 電子の強い相関が本質的に重要であり，$BaBiO_3$ と同様な近藤系と見なせること，又その磁性は近藤系に誘起されたもので Ba の置換により 3 d(z^2) −p 反結合バンド上に生ずるホールにより増強された近藤効果が磁性を壊し，f-電子系の重い電子超伝導と同様の機構が高温超伝導を引き起こしたものと考えられる。

$BaPb_{1-x}Bi_xO_3$ system shows very unusual physical properties even though only s-p bands exist near around Fermi energy. Detailed band calculations have been done on this system and the following conclusion was obtained. The usual band calculation seems to be applicable on $BaPbO_3$ with the well known modification that the unoccupied s-p anti-bonding band is shifted up from the non-bonding p bands with a gap of 1 eV. Existing $BaPbO_3$ samples are thought to have a few percents of O-vacancies. On the other hand in $BaBiO_3$ a strong correlation energy in the Bi 6s electrons becomes important and the model with one 6s electron on each Bi becomes a good starting picture. The Kondo state in a wide sense is thought to cause the observed nonmagnetic character. The insulator transition at 30% Bi substitution is due to the dominating 6s correlation effect in Bi and the high T_c value is due to the enhanced electron-phonon interaction. Various band calculations for La_2CuO_4 were also done and the same starting picture in which the 3d(x^2-y^2) electrons are treated as the strongly correlated state was obtained. Decreasing magnetism with increasing Ba doping is due to increasing Kondo temperature with the increasing of the valence electrons and the mechanism of the superconductivity is thought to be the same as that of the heavy fermion system.

The alloy system $BaPb_{1-x}Bi_xO_3$ $(0<x<1)$ shows very unusual physical properties which contradict the usual band pictrue even if only the wide s and p electron bands are concerned. The usual band calculation done for $BaPbO_3$ shows the following character.[1] The bands near the Fermi level are formed mainly from the 6s electrons of Pb and the 2p electrons of O. At the Γ-point these states are of nearly the same energy as average but except the Γ-point they show a strong s-p bonding and anti-bonding effect causing the largest splitting of 15 eV at the R-point. On the other hand the non-bonding p-bands are of dispersionless existing below the Fermi energy. The anti-bonding band overlaps a little bit with the non-bonding p bands and thus the system is expected to be semimetal in agreement with experiments.[2] A big disagreement exists, however, with the photoemission spectra, PES.[3,4] The band theory shows a fairly large density of states of non-bonding p-bands at and below the Fermi level but PES shows very weak intensity at and below the Fermi level down to 1.5 eV. Various improvements were done on the usual band calculation. However, as far as we agree that the system is intrinsic semimetal, the contradiction with PES can not be removed. The only solution on this point for the band model is as follows. It is well known that the usual band calculation shows too narrow energy gap between the occupied and unoccupied bands because of the inadequate treatment of the self-interaction energy.[5] Therefore, it is rather naturally expected that there is a gap between the unoccupied anti-bonding and the occupied non-bonding bands. It is also well known that it is very difficult to grow a good stoichiometric $BaPbO_3$ sample and all the existing samples are of high residual resistivity with substantial amount of O-vacancy, a few percents. Therefore the existing $BaPbO_{3-y}$ samples are thought to be not semimetal but degenerate semiconductor with a gap of 1 eV. As Pb is replaced by Bi, the number of conduction electron increases nearly proportionally with the Bi concentration x in agreement with experiment. Furthermore, the system becomes superconductor. However, when x increases beyond about 0.3, the system becomes insulator suddenly. This is very unusual because the anti-bonding s-p band is fairly wide, about 8 eV. The insulating character becomes strongest in $BaBiO_3$ and thus now we consider this material.

The band structure for $BaBiO_3$ is essentially the same as that for $BaPbO_3$ except that the s band energy at the Γ-point is about 3.5 eV lower relative to the p-bands and the anti-bonding band is half-filled.[1] Because of the excellent nesting character of the half-filled band, the transition to the charge density wave state was thought to be the origin of the insulator character.[6] However, various experimental results are negative to this mechanism. For examples, core excitation spectra[3,4] see only one kind of Bi state and detailed neutron scattering measurement[7] does not show any significant breathing mode distortion of oxigen which is expected for CDW state. Our band calculations are also negative for CDW insulator. The largest charge ordering is expected in the ordered alloy $BaPb_{0.5}Bi_{0.5}O_3$ but even in this case the CDW gap is nearly zero.[1] As another example, the CDW state for a large breathing mode distortion, the distances between Bi1-O and Bi2-O are 2.262 Å and 2.088 Å, respectively, much larger than the measured values, is shown in Fig. 1. Even in such a large distortion, no CDW gap is obtained.

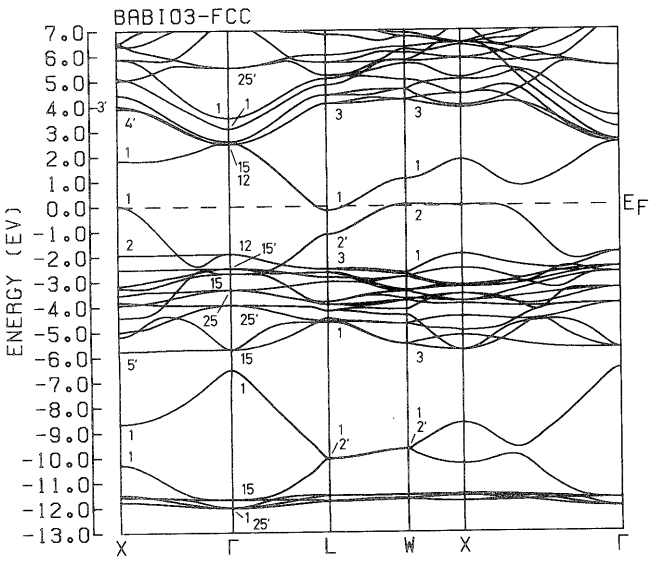

Fig. 1. Band structure of $BaBiO_3$ with the breathing mode distortion as described in the text.

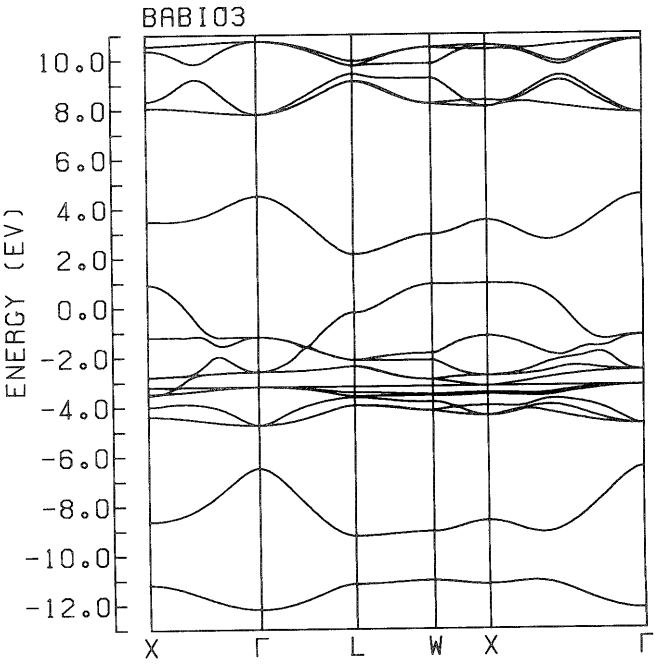

Fig. 2. LCAO-band structure of antiferromagnetic $BaBiO_3$ as described in the text. Antiferromagnetic exchange potential has a stronger effect on the bonding s–p band. The different s–p mixing for the majority and minority spin 6s electrons has important effect for the gap formation in the anti-bonding s–p band.

Persistent and weak alloy dependent gap for $0.3<x<1$ strongly suggests that the gap formation is due to the strong correlation effect of the 6s electron. Actually the atomic optical data show that the correlation energy of the 6s electron is large, about 10 eV.[8] Furthermore, because the 6p bands are far away from the Fermi level, the screening effect is small. Note that the correlation energy of the oxygen 2p is larger, about 14 eV,[8] but because of the large degeneracy the screening effect is strong in the crystals. The easiest way to take into account the correlation energy in the crystal is to perform the band calculation in the antiferromagnetic configuration. Such a calculation were done but the antiferromagnetic state was found to be unstable. This is, however, due to mostly inadequate exchange-correlation potential in the usual band calculation. To take into account the correlation effect in maximum, we performed the band calculation of LCAO in which various parameters were determined to fit the results of the previous APW band calculation[1] and the correlation energy was chosen to be 10 eV. Furthermore the ratio of the s–p mixings for the majority and the minority 6s electrons is chosen to be 0.85. The result is shown in Fig. 2. Now we have a gap of 1 eV with the local moment of about $0.5\,\mu_B$. However, the result depends sensitively on the chosen parameter values and the gap in Fig. 2 seems to be maximum. Anyway, the ionic model of the tetravalent Bi, in which each Bi contains one 6s electron seems to be a good starting model. In this model, one oxygen vacancy creates two trivalent Bi at the nearest neighbour with the $6s^2$ configuration while a Pb substitution simply shows a tetravalent Pb of $6s^0$, keeping the system insulator. A more interesting alloying is the substitution of La and Cs for Ba.

A remaining question is whether $BaBiO_3$ is antiferromagnet or not. There are no conclusive experimental results on this poit but non-magnetic state seems to be more probable. Recently Anderson proposed the RVB model claimed to be suitable to the present case as well as the Kondo lattice case.[9] However, his model of singlet formation by two site mixing is different essentially from the Kondo singlet formation by single site mixing. Recently our experimental group found that the concept of Kondo lattice is more widely applicable in various materials in which the number of conduction electrons is very small or even in insulator with a small gap.[10,11,12] It may be understood naturally that at least for the magnetic properties there are no essential change even if a gap which is substantially smaller than the Kondo temperature is formed at the Fermi level. In this sense $BaBiO_3$ seems to be similar to Sm_3Se_4 in which the 4f levels are situated within the gap of conduction and valence bands but very near the bottom of the conduction band and the heavy fermion like behavior is observed.[13] In the present case the 6s electrons correspond to the f electrons and the non-bonding 2p bands to the conduction bands. Due to the large s–p mixing the Kondo temperature seems to be several thousands degrees.

Now we return to the small substitution of Bi for Pb. For a small substitution range of Bi, the usual band picture seems to be applicable. However, as the Bi content increases, the strong correlation effect on Bi sites becomes important and the system changes to the insulating phase. The high superconducting transition temperature, $T_c \sim 10$ K, is thought to be due to the enhanced electron-phonon interaction. Due to the near critical region for the insulating state the band energy is expected to show a larger energy shift for a lattice distortion, in particularly for the breathing mode. Actually some softening of the breathing mode is observed.[14] Detailed numerical calculation is, however, not yet done in the present system because of the large ambiguity to treat the 6s correlation energy as mentioned before. Instead of the present system, some estimation was done on La_2CuO_4 because the 3d correlation effect is known much better.

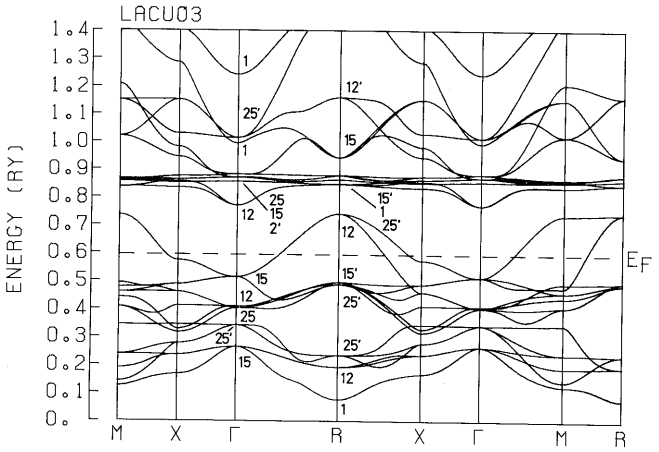

Fig. 3. Band structure of $LaCuO_3$ for the ideal perovskite structure. The narrow bands at 0.85Ry are due to La 4f states.

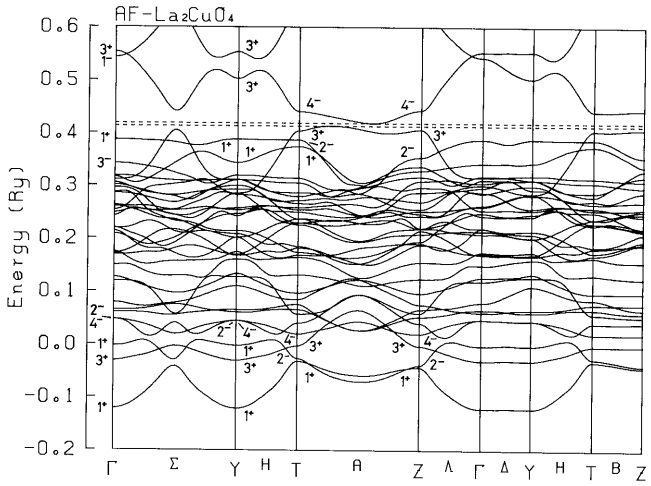

Fig. 4. Band structure of antiferromagnetic La_2CuO_4 in which the exchange potential for Cu-d bands is doubled.

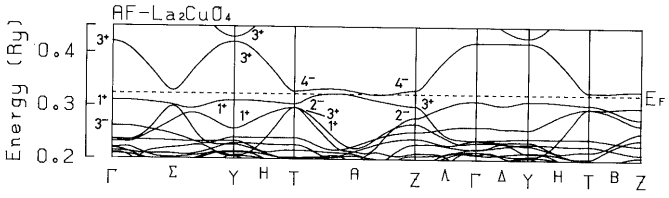

Fig. 5. The same as for Fig. 4 but with the expanded lattice as described in the text. Note that the $d(x^2-y^2)$-p anti-bonding band is shifted down compared with other bands, in which the $d(z^2)$-p anti-bonding band has the maximum.

The band scheme of La_2CuO_4 is very similar to that of $BaBiO_3$.[15] To see the relation better, we performed the band calculation also for the ideal perovskite structure of $LaCuO_3$ as shown in Fig. 3.[16] For the s-p bands, the s-p bonding band is the lowest but the s-p anti-bonding band is well above the Fermi level because the Cu 4s band energy at the Γ-point is well above the Fermi level. Instead of the 4s electrons, the Cu 3d electrons are now nearly degenerated with the O 2p electrons. Now, corresponding to the doublet character of $d\gamma$ states, doubly degenerated d-p bonding and anti-bonding bands are formed and other d and p bands form narrow non-bonding bands. Because of the smaller 3d-2p mixing, the overall band splitting at R-point, R_{12}, is about 7.5 eV, half of that in $BaBiO_3$. The band structure of the layered perovskite La_2CuO_4 is very similar with that of $LaCuO_3$. The only main difference is that now due to the layered structure the $d(x^2-y^2)$-p anti-bonding is much larger than the $d(z^2)$-p anti-bonding and thus the Fermi level cut the middle of the former anti-bonding band, showing an excellent two dimentional nesting due to the two dimentional band character. Again, however, a CDW state is not observed and the correlation effect seems to be more important. Actually the atomic correlation energy in the 3d electrons is large, more than 20 eV.[8] In the crystal, however, due to the 4s and other 3d electrons screening effect, the effective correlation energy is evaluated to be about several eV. This means that the ratio of the correlation energy to the anti-bonding band width is also very similar to that of $BaBiO_3$. La_2CuO_4 is, however, magnetic insulator and thus we tried to calculate the antiferromagnetic state by the usual band scheme. Again, however, we failed to obtain the stable antiferromagnetic state due to the inadequate exchange-correlation potential in the usual scheme even in the 3d electrons. This inadequancy was most clearly shown already in the spin wave calculation in Ni and Fe.[17] The main origin of the failure is again due to inadequate treatment of the self-interaction term and there are various ways to treat this problem. Here we simply multiplied the exchange term so as to get the sublattice magnetization consistent with the experimental result. Then, by doubling the exchange term, we obtained the antiferromagnetic state with the sublattice magnetization of 0.4 μ_B. The band structure is shown in Fig. 4. To see the electron-phonon interaction, the crystal was expanded uniformly along the c-plane by 5%. The result is shown in Fig. 5. Contraly to our expectation, the gap energy shows nearly no change. However, the total band width changed substantially due to the weaker d-p mixing and the Fermi energy decreased about 1 eV relative to the center of the non-bonding bands. This gives the electron-phonon coupling energy. The breathing mode should cause a large change in the energy gap but such a calculation is not yet performed.

Similar to $BaBiO_3$ the inoic model of divalent Cu with one 3d hole seems to be the better starting model for the magnetic insulating state. In this picture, the top of the occupied band is that of the $d(z^2)$-p anti-bonding band and the $d(x^2-y^2)$ electrons are treated as the strongly correlated localized states in the same way as the 6s electrons in $BaBiO_3$. Then again the situation is exactly same as that in $BaBiO_3$ except the layered character. La_2CuO_4 is evaluated as the antiferromagnetic state induced on the Kondo lattice in the wide sense mentioned before. When La is replaced by a small amount of divalent atoms, the holes are induced at the top of the valence bands, which causes a stronger Kondo state and thus weaker magnetism and finally the system becomes non-magnetic Kondo lattice state. The superconductivity should be understood as the heavy fermion superconductivity similar to those of the f-electron system. The detail of the mechanism will be shown in the forthcoming paper.

Acknowledgments

The numerical computation was performed by the use of the ACOS-1000 and SX-1 computer at the Computer Center of Tohoku University and the HITAC M-680H and S810/10 computer at the Computer Center of the Institute for Molecular Science, Okazaki National Research Institutes.

References

1) K. Takegahara and T. Kasuya: J. Phys. Soc. Jpn. **56** (1987) 1478.
2) S. Uchida, K. Kitazawa and S. Tanaka: Phase Transitions **8** (1987) 95.
3) G. K. Wertheim, J. P. Remeika and D. N. E. Buchanan: Phys. Rev. **B26** (1982) 2120.
4) H. Sakamoto, H. Namatame, T. Mori, K. Kitazawa, S. Tanaka and S. Suga: J. Phys. Soc. Jpn. **56** (1987) 365.
5) W. E. Pickett: Comments Solid State Phys. **12** (1985) 1, 57.
6) L. F. Mattheiss and D. R. Hamann: Phys. Rev. **B28** (1983) 4227.
7) C. Chaillout, J. P. Remeika, A. Santoro and M. Marezio: Solid State Commun. **56** (1985) 829.
8) C. E. Moore: *Atomic Energy Levels* (Circular of the National Bureau of Standards 467, Washington D.C., 1949, 1952, 1958) Vols. I–III.
9) G. Baskaran and P. W. Anderson: Phys. Rev. **B37** (1988) 580.
10) A. Ochiai, K. Takeuchi, N. Niitsuma, T. Suzuki and T. Kasuya: J. Magn. Magn. Mater. **63 & 64** (1987) 618.
11) Y. S. Kwon, A. Ochiai, H. Kitazawa, N. Sato, H. Abe, T. Nanba, M. Ikezawa, K. Takegahara, O. Sakai, T. Suzuki and T. Kasuya: J. Magn. Magn. Mater. **70** (1987) 397.
12) A. Ochiai: Dr. Thesis, Faculty of Science, Tohoku University, Sendai, 1988.
13) A. Tamaki, T. Goto, S. Kunii, T. Suzuki, T. Fujimura and T. Kasuya: J. Phys. C: Solid State Phys. **18** (1985) 5849.
14) W. Reichardt and W. Weber: Jpn. J. Appl. Phys. **26** (1987) Suppl. 26-3, 1121.
15) K. Takegahara, H. Harima and A. Yanase: Jpn. J. Appl. Phys. **26** (1987) L352.
16) K. Takegahara: Jpn. J. Appl. Phys. **26** (1987) L437.
17) J. F. Cooke, J. A. Blackman and T. Morgan: Phys. Rev. Lett. **54** (1985) 718.