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Submitted to 7th International Conference on Solid State Ionics (SSI-7), Hokone, Japan, November 5-11, 1989.

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# Superconductivity in $Ba_{1-x}K_xBiO_3$

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Phonon density-of-states(DOS) of insulating $BaBiO_3$ and superconducting $Ba_{0.6}K_{0.4}BiO_3$ is studied using effective interaction potentials and molecular dynamics(MD) method. MD results are in good agreement with the inelastic neutron scattering and electron tunneling experiments. Calculated oxygen isotope effect using the Eliashberg gap equations is also in good agreement with the experiments. Cumulative evidence based on the neutron scattering, tunneling, and the isotope effect suggests that this material is a normal BCS electron-phonon superconductor.

**Key Words:** High $T_c$ Superconductors, Isotope Effect, Neutron Scattering, Molecular Dynamics Simulations.



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## 1. Introduction

Discovery of superconductivity at ~30K in $Ba_{1-x}K_xBiO_3$ for $0.25<x<0.50$ is of great interest because of the difference between this material and other high-$T_c$ oxides.[1,2] Even though all the superconductors with transition temperatures greater than 30K are oxides, they are different because $Ba_{1-x}K_xBiO_3$ is cubic whereas others have planar structures. The undoped insulating material is monoclinic( distortion from the orthorhombic structure used in MD is very minute), but superconducting $Ba_{1-x}K_xBiO_3$ is cubic. In contrast, the higher $T_c$ oxide superconductors have Cu-O planes and chains. Furthermore $Ba_{1-x}K_xBiO_3$ shows none of the antiferromagnetism exhibited by the undoped layered high-$T_c$ materials. Infrared measurements of the superconducting gap in $Ba_{0.6}K_{0.4}BiO_3$ give $2\Delta = 8.7$ meV and $2\Delta/k_BT_c \approx 3.5$.[3] Isotope effect measurements by Hinks et al. for $^{16}O$ to $^{18}O$ substitution in $Ba_{0.6}K_{0.4}BiO_3$ give a value of $\alpha = 0.41\pm0.03$ ($T_c \sim M_O^{-\alpha}$).[4] A lower value $\alpha = 0.22\pm0.03$ is found by Batlogg et al..[5] Kondoh et al. finds a value $\alpha = 0.35\pm0.05$.[6] A value of $2\Delta/k_BT_c \approx 3.5$ and large isotope effect suggest that $Ba_{0.6}K_{0.4}BiO_3$ may be a weak coupling superconductor in which phonons play an important role.

## 2. Structural Information and $T_c$ versus Composition

Phase diagram of $Ba_{1-x}K_xBiO_3$ along with the behavior of $T_c$ with K concentration[7] are shown in Fig. 1. Main points to note are that for $x< 0.25$ the material is insulating and around $x = 0.4$ it is cubic and the $T_c$ is practically constant.

## 3. Molecular Dynamics Simulations

Effective interparticle interactions were used in the molecular dynamics simulations. The potentials include steric repulsions between ions, Coulomb interactions due to charge transfer effects, and charge-dipole interactions due to large electronic polarizability of $O^{--}$ ions. The calculations

experimental number density. The structural parameters used in the MD simulations are found in Table I. The $Ba_{0.6}K_{0.4}BiO_3$ system was obtained from $BaBiO_3$ by randomly replacing 40% of the Ba atoms with K atoms. Before calculating the phonon DOS, it was ensured that the systems were dynamically stable in the appropriate symmetries. The phonon DOS was calculated using three methods: (1) from the Fourier transform of the velocity auto-correlation functions, (2) the equation of motion method, and (3) direct diagonalization of the dynamical matrix. The results of all these three calculations are in good agreement with one another.

**4. Phonon Density of States**

Generalized neutron DOS,[8] and molecular dynamics results for total and partial phonon DOS in $BaBiO_3$ and $Ba_{0.6}K_{0.4}BiO_3$ are shown in Figs. 2 and 3, respectively.

In $BaBiO_3$ the phonon density of states from neutron scattering shows peaks at 35, 43, 63, and 71 meV. The main peaks in the MD result occur at 25, 32, 37, 45, 51, 60, 66, and 74 meV. The two peaks at 11 and 16 meV in the MD result are not observed in the neutron measurement because of low-energy cutoff in the experiments. In $Ba_{0.6}K_{0.4}BiO_3$ the phonon spectrum broadens and shifts to lower energies due to K doping and is comprised four significant features, 1) a band extending from 25 to 37 meV, 2) a peak around 51 meV, 3) a band between 54 and 65 meV, 4) small peaks at 67 and 73 meV. Results of MD simulation are in good agreement with the recent inelastic neutron scattering experiments by Loong et al.[8] To understand the origin of the peaks in the DOS, we examine the MD results for the partial phonon DOS in Figs. 2 and 3. There is a clear delineation in the peaks associated with Ba, K, Bi on one hand and O on the other. Phonons below 20 meV are due to vibrations of Ba, K, and Bi atoms. Above 20 meV the entire spectrum arises from oxygen vibrations.

**5. Electron Tunneling Experiments**

Electron tunneling experiments on S-I-S and S-I-N junctions were

carried out by Zasadzinski et al..[9] All significant features in the MD DOS and neutron generalized DOS are seen in the tunneling measurements. MD calculations reveal that the 35 and 60 meV phonons arise from symmetric breathing modes of oxygen vibrations around Bi(~ 35 meV), and Ba and K(~60 meV), respectively. Neutron and tunneling experiments together with MD simulations suggest coupling of carriers to oxygen breathing modes around 35 and 60 meV.

## 6. Isotope Effect due to $^{16}O$ to $^{18}O$ substitution

Isotope effect was calculated from the $^{16}<\omega>$ and $^{18}<\omega>$ and also by directly solving the Eliashberg Gap Equations[10] to determine the $^{16}T_c$ and $^{18}T_c$. Results of these calculations are summarized in Table II. With $F(\omega)$ denoting the phonon density of states

$$<\omega> = \int \omega F(\omega) d\omega \; / \int F(\omega) d\omega \; .$$

Implications of the strong coupling effects are studied within the Eliashberg theory with a model of $\alpha^2(\omega)F(\omega)$ which is consistent with the electron tunneling experiments.

## 7. Conclusions

MD simulations in conjunction with the neutron, tunneling, infrared, and isotope effect measurements reveal that $Ba_{0.6}K_{0.4}BiO_3$ is a weak coupling superconductor in which the carriers have a strong matrix element to high frequency oxygen vibrations.

**Acknowledgements**

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**Table I:** Experimental data used in the MD simulations.

| | $BaBiO_3$ | $Ba_{0.6}K_{0.4}BiO_3$ |
|---|---|---|
| $T_c$[4] | - | 29.5K |
| Mass density | 7.88 | 7.33 g/cm$^3$ |
| Lattice[11] | orthorhombic<br>a=6.2000<br>b=6.1561<br>c=8.6948 | cubic<br>a=4.3160Å |

**Table II:** The first moment of the phonon density of states from MD for isotopes of oxygen in meV, $T_c$ the temperature below which the resistivity is zero, and $\alpha$ the isotope exponent. The value of $T_c$ for $^{16}O$ is from experiment[4] and the one for $^{18}O$ from Eliashberg equations.

| | $\langle\omega\rangle$ | $T_c$(K) |
|---|---|---|
| $^{16}O$ | 33.50 | 29.5 |
| $^{18}O$ | 31.91 | 28.1 |
| $\alpha$ | 0.41 | 0.38 |

**Figure Captions**

Figure 1 Phase diagram for $Ba_{1-x}K_xBiO_3$ and $T_c$ versus concentration of K.[7]

Figure 2 Density of states for $BaBiO_3$ from neutron experiment and MD simulations(total and partials).[8]

Figure 3 Density of states for $Ba_{0.6}K_{0.4}BiO_3$ from neutron experiment and MD simulations(total and partials).[8]

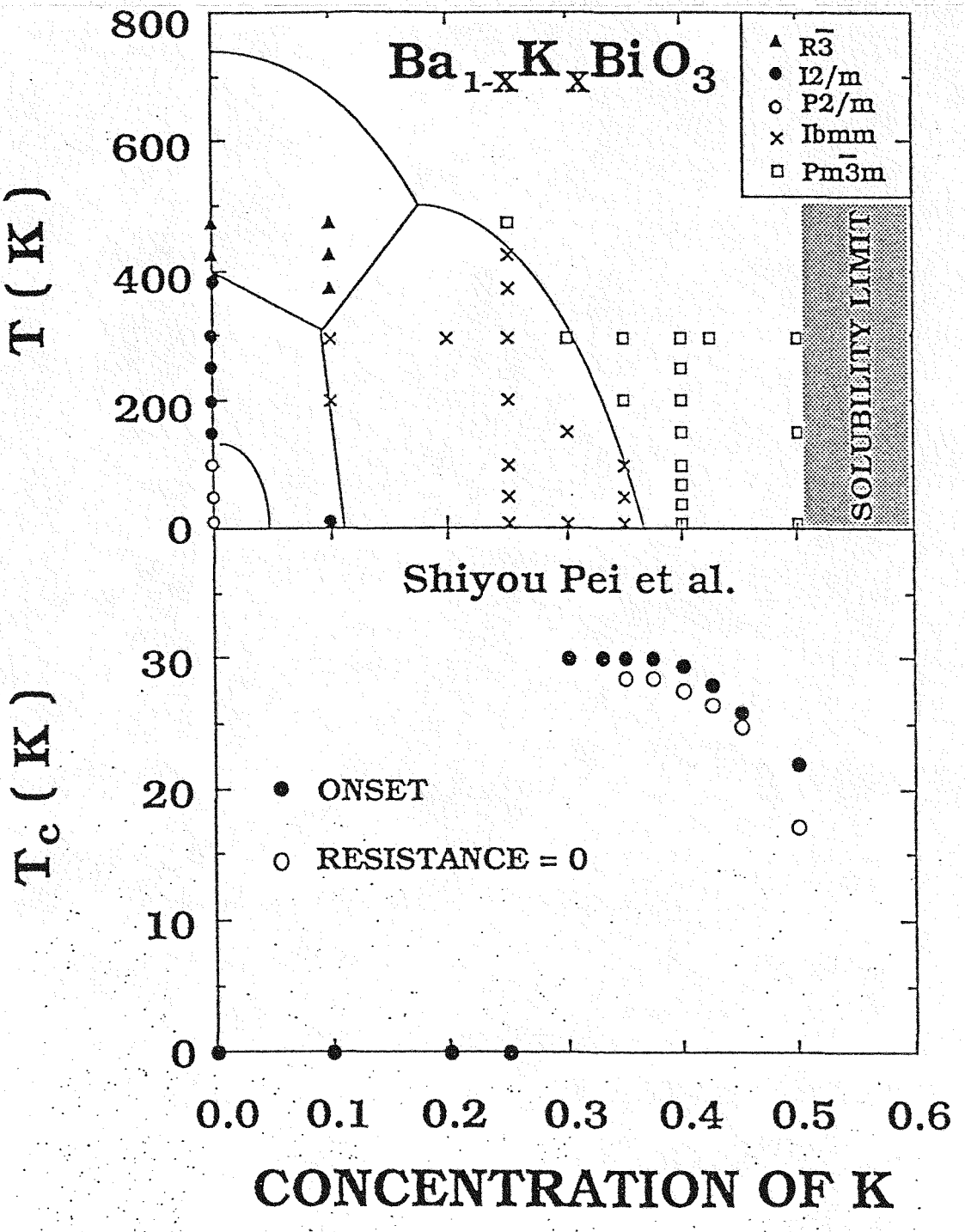
$Ba_{1-x}K_xBiO_3$
R3̄
I2/m
P2/m
Ibmm
Pm3̄m
SOLUBILITY LIMIT
T ( K )
800
600
400
200
0
Shiyou Pei et al.
$T_c$ ( K )
30
20
10
0
ONSET
RESISTANCE = 0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
CONCENTRATION OF K

Fig 1

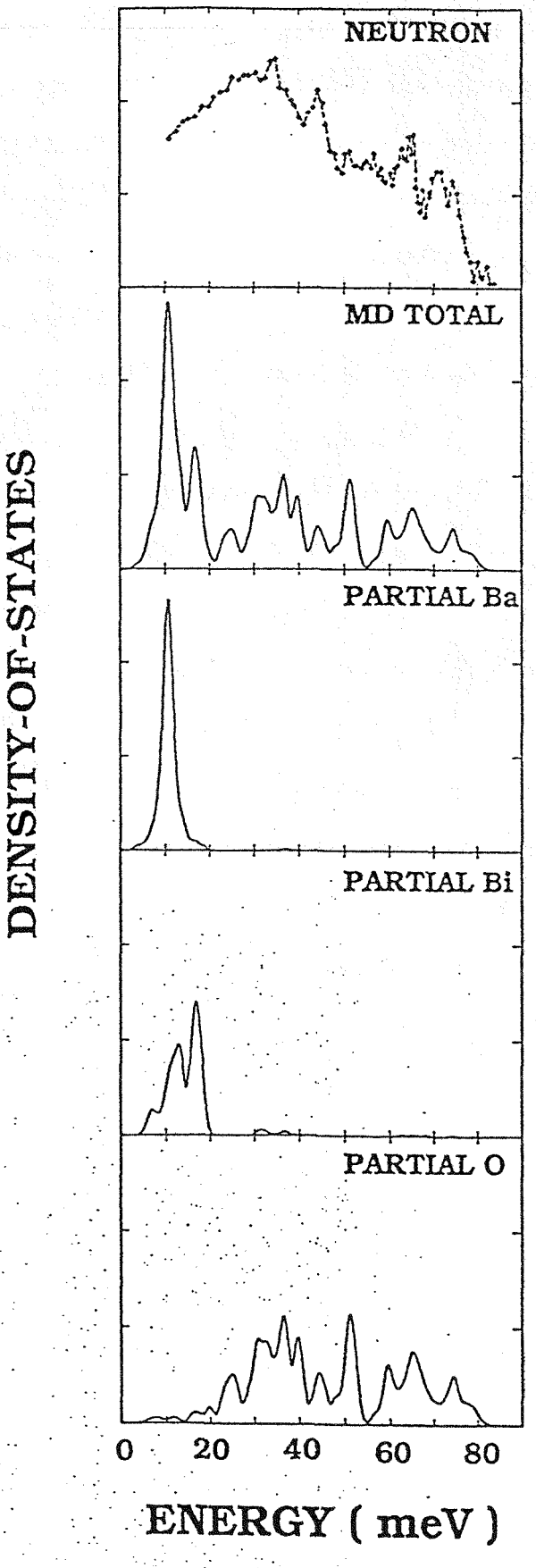
NEUTRON
MD TOTAL
PARTIAL Ba
PARTIAL Bi
PARTIAL O
DENSITY-OF-STATES
0
20
40
60
80
ENERGY ( meV )

Fig 2

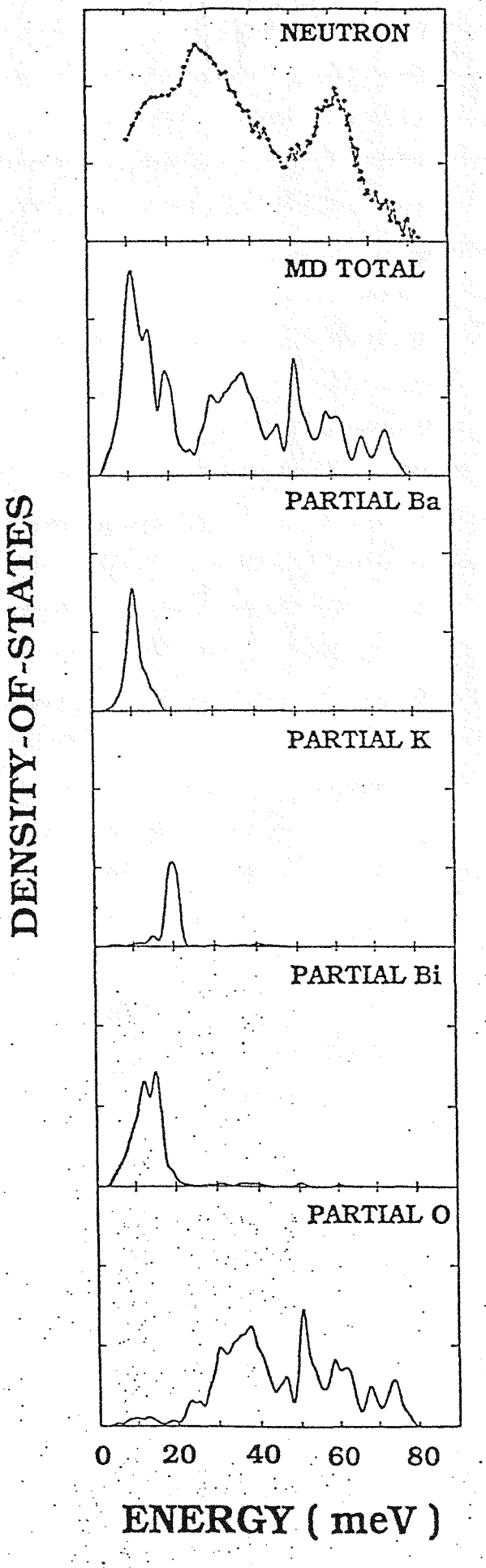
NEUTRON
MD TOTAL
PARTIAL Ba
PARTIAL K
PARTIAL Bi
PARTIAL O
DENSITY-OF-STATES
0
20
40
60
80
ENERGY ( meV )

Fig 3