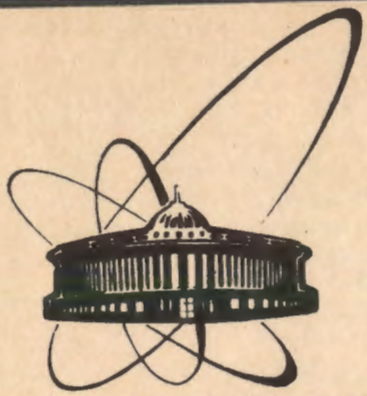

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LATTICE DYNAMICS OF $Ba_{1-x}K_xBiO_3$ AS STUDIED BY NEUTRON SCATTERING AND COMPUTER SIMULATION

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1 Introduction

The discovery of superconductivity in $Ba_{1-x}K_xBiO_3$ (BKBO) [1-3] has attracted attention of physicists despite of relatively low critical temperature, $T_c = 30K$, in comparison with other high temperature superconductors. Unlike copper oxides, the BKBO superconducting phase is a simple cubic perovskite [2, 4, 5] without metal-oxygen planes which play an important role in the superconductivity of the other $High - T_c$ materials. Measurements with magnetic methods [6] have revealed no magnetic ordering in the compound. Measurements of the Hall constant [6] have shown that in BKBO the electrons of small effective mass are the charge carriers and not the large effective mass holes as in cuprates.

At the same time this compound posesses some properties which are common for other perovskite superconductors. So the parent compound $BaBiO_3$ is an insulator and superconductivity in BKBO arises near the dielectric–metal phase transition point [2, 7] due to doping with lower valency ions similarly to the $La_{2-x}(Sr, Ba)_xCuO_4$ system. Magnetic properties of BKBO are irreversibile, which fact finds no explanation in the flux–creep model, [8]. The electron correlation length is small [9] which is characteristic of all perovskite superconductors.

Therefore, a detailed study of BKBO properties could be useful for understanding the nature of high temperature superconductivity.

Experimental and theoretical data recently obtained provide evidence for the important role that phonons play in the mechanism of structural phase transitions and superconductivity in BKBO. The study of the oxygen isotope effect $^{16}O - ^{18}O$ on the superconducting transition temperature yielded the results in agreement with the phonon mechanism [6, 3, 11]. Measurements on heat conduction [12, 13] have also demonstrated the heat conductivity behaviour similar to conventional superconductors. The superconducting gap measured in the experiments on the determination of lower and upper critical fields [11] and by the method of infrared reflection [14] was found to be $2\Delta/T_c = 3.5$ in agreement with BCS predictions. The tunneling experiments gave the value of 3.75–3.9 [15, 16, 17] for the energy gap and $\lambda \simeq 1$ for the electron-phonon interaction constant. The temperature dependence of the energy gap is in good agreement with the BCS theory [15].

A strong electron–phonon interaction was proposed to explain some peculiar features of BKBO. Electronic structure calculations [19] have demonstrated that one could expect the strongest electron–phonon interaction for the breathing modes of oxygen octahedra. Under assumption that the local breathing modes of oxygen atoms are responsible for the charge density wave instability near the dielectric–metal phase transition point, an increase in superconducting transition temperature in this point was explained [20, 21]. A number of earlier experiments [7, 22] have also evidenced in favour of the existence of these fluctuations. The study of lattice dynamics and BKBO superconducting properties in the frame of the model of strong electron coupling with oxygen breathing modes [23] has allowed one to obtain good agreement with experimental superconductive transition temperature, its dependence on potassium concentration, isotope effect and the value of the superconducting gap.

The present work was aimed at the study of $BaBiO_3$and $Ba_{0.6}K_{0.4}BiO_3$ lattice dynamics on the basis of a simple model of interatomic potential and by inelastic neutron scattering. Section 2 of this paper summarizes the results of theoretical calculations and their comparison with experiment. Section 3 describes the sample preparation procedure, sample testing and the details of the neutron scattering experiment. In Section 4 the experimentally obtained generalized density of phonon states is compared with the results of calculation. Section 5 presents general conclusions.

2 Theory

Lattice dynamics of a parent compound $BaBiO_3$ was considered in cubic symmetry using a unit cell parameter $a = 4.29$Å. The interatomic potential function was assumed to consist of the Coulomb term and a soft core repulsive term:

$$V_{ij} = \frac{Z_i Z_j e^2}{R_{ij}} + a_{ij} \exp(-b_{ij} R_{ij}).$$

Here Z_i is the effective valency of the ion i , R_{ij} the distance between the ions i and j, a_{ij} and b_{ij} the fitting parameters. We accepted Ba^{2+}, Bi^{4+}, O^{2-} ion valencies. The interatomic distances were calculated for a cubic phase (space group $Pm\bar{3}m$ [7]) having the above cited unit cell parameter. The parameters a_{ij} and b_{ij} were considered to be different from zero only for oppositely charged ions, that is for the pairs $Bi-O$ and $Ba-O$. As the result we have four free parameters to be fitted to experimental data. The first two conditions followed from the requirement that crystal energy has to be minimized with respect to crystal lattice parameters. As the other conditions we have chosen the experimental phonon frequencies in the center of the Brillouin zone. Unfortunately a complete set of optical frequencies for $BaBiO_3$ does not exist and it made us to take their values from works on $Ba(Pb,Bi)O_3$ [24, 25] : 70 meV, 24.3 meV, 23.8 meV and 15 meV. The value for the upper frequency is in good agreement with the published results on the light scattering in $Ba_{0.6}K_{0.4}BiO_3$, where it was assigned to the breathing mode of BiO_6 octahedra [26, 27]. Therefore, one assumes that the values for the other frequencies cannot be much different. Thus we have six conditions for the determination of four parameters. This problem was solved with the WMIN program [28] and the following values for the phonon frequencies in the center of the Brillouin zone were obtained: 72 meV, 31 meV, 26 meV and 13 meV. Potassium doping in the $Ba_{0.6}K_{0.4}BiO_3$ was taken into account through corresponding mass and valency changes for the Ba ion and valency changes for the O ion to meet the requirement of charge neutrality. The parameters of the potential for $Ba-O$ were changed in correspondence with the crystalline structure equilibrium condition. At a 40% level of doping, the system reveals a metallic behaviour. Nevertheless, the use of the chosen potential seems justified here due to small electronic density of states near the Fermi energy and low charge carriers concentration in this system [11, 6].

Dispersion curves calculated for the [100], [110] and [111] directions in the Brillouin zone have demonstrated that the $BaBiO_3$ cubic lattice appeared unstable with respect to the libration mode of BiO_6 octahedra along [110] and [111] directions. Figure 1a shows the dispersion curves along [100] and [111] directions. For the sake of clarity only acoustic branches and the unstable libration mode are shown there. Figure 1b shows the dispersion curves for the same directions in $Ba_{0.6}K_{0.4}BiO_3$. One can see that potassium doping leads to cubic lattice stabilization. An analogous result was obtained for the [110] direction.

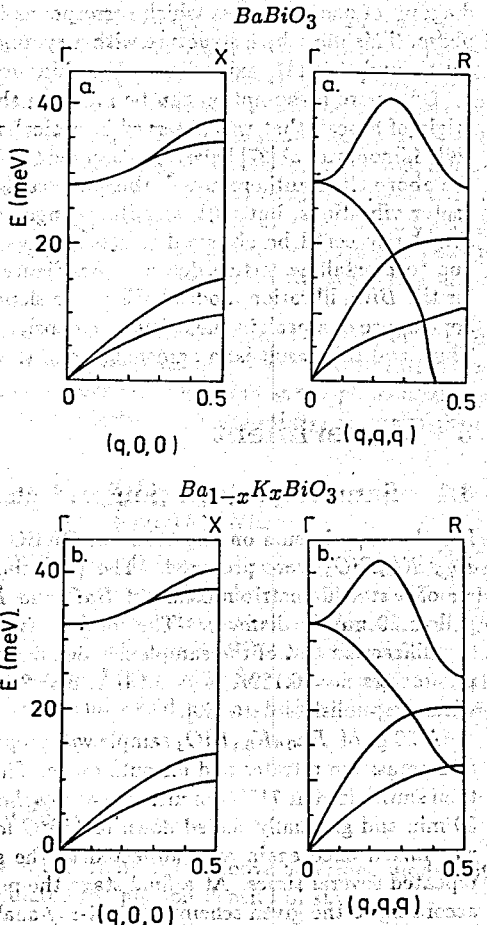


Fig.1.
Calculated phonon dispersion curves for $BaBiO_3$ (a) and $Ba_{0.6}K_{0.4}BiO_3$ (b). For the sake of clarity only acoustic and BiO_6 libration modes are shown. One can see that, while in the (q,0,0) direction, lattice dynamics is stable for both systems, in the (q,q,q) direction the cubic phase of $BaBiO_3$ is unstable with respect to BiO_6 tilt. The same is true for (q,q,0).

Analysis of the results allows one to make some conclusions. The study of the phase diagram for this system [7] showed that the cubic phase $Pm\bar{3}m$ transforms into the orthorhombic phase $Ibmm$ with decreasing potassium concentration at temperatures below 500K. This phase transition is connected with BiO_6 octahedron rotation around the [110] axis and along this direction our calculations have revealed instability of the cubic phase

of $BaBiO_3$. At temperatures above 500K the cubic phase transforms into the rhombohedral $R\bar{3}$ phase with decreasing potassium concentration. This transition is due to combined rotation of the BiO_6 octahedron around the [111] axis and breathing mode distortions. Instability of the cubic lattice of $BaBiO_3$ along the [111] direction obtained in our calculations is, therefore, also in agreement with experiment.

In addition these calculations have allowed us to assume the existence on the phase diagram of one more area which corresponds to an intermediate between $Pm\bar{3}m$ and $R\bar{3}$ phase. This must be a structure with a symmetry $R\bar{3}c$, which contains a rigid octahedral tilt around the [111] axis with no breathing mode distortion.

One more presumption can be made on the basis of our calculations, concerning the origin of a peak that was observed in optical spectra at a frequency of $348cm^{-1}(43meV)$ [26]. Limonov et al [27] have also observed this peak, but at somewhat lower frequency. As the above cited authors noted, this peak could be not connected with the Brillouin zone center vibrations, but with van Hove singularity in the phonon density of states. This singularity could be observed in Raman spectra because of the selection rule violation due to crystalline lattice defects. As Figure 1 shows the calculated dispersion curves for the BiO_6 libration modes have a zero slope at about 40 meV, which fact leads to the appearence of a peak in the calculated density of phonon states near the energy indicated. Thus, and this result is in agreement with the known experimental facts.

3 Experiment

3.1 Sample preparation and characterization

For the experiments on the study of BKBO lattice dynamics samples of $BaBiO_3$ and $Ba_{0.6}K_{0.4}BiO_3$ were prepared. The potassium free sample was produced by firing in air of a stoichiometric mixture of BaO and Bi_2O_3 with the product then pressed into pellets 60 mm in diameter. The total mass of the sample amounted to 180 g. The X-ray diffraction test of the sample has demonstrated no impurity phases and gave the cell parameters $a = 6.182$Å, $b = 6.137$Å, $c = 8.660$Å and $\beta = 90.173°$, in good agreement with the published data [30].

A 20 g. of $Ba_{0.6}K_{0.4}BiO_3$ sample was prepared from stoichiometric mixture of barium and potassium nitrates and bismuth oxide. The starting composition carefully mixed was then sinthesized at $715°C$ in nitrogen atmosphere, kept in oxygen atmosphere at $450°C$ for 30 min and gradually cooled down to $150°C$ for 5 hrs. in oxygen flow. Then the powder was mixed once again and subjected to the same process of sythesis. This procedure repeated several times. At a final stage the powder was pressed into pellets and treated according to the given scheme. The X-ray analysis showed the presence of a single phase having a cubic unit cell parameter $a = 4.28$Å. By measuring temperature dependences of resistivity and magnetic susceptibility we have found the superconducting transition temperature $T_c = 28K(\Delta T_c = 3K)$.

3.2 Neutron scattering experiment

In neutron scattering experiments samples sealed in flat aluminium cans were placed in a cryostat. The measurements were performed at sample temperatures: 10K, 80K and 290K.

Inelastic neutron scattering experiments were carried out on the inverted geometry spectrometer KDSOG-M at the IBR-2 reactor of the JINR [31] and on the direct geometry spectrometer of the Kurchatov Institute of Atomic Energy (IAE) [32]. The inverted geometry spectrometer exploited the white neutron beam from the pulsed reactor. Energies of incident neutrons were determined by measuring neutron time of flight from source to sample. Their final energy of 5 meV was kept fixed with the help of a liquid nitrogen cooled beryllium filter and single crystals of pyrolytic graphite. The neutron energy loss spectra were measured simultaneously for eight scattering angles: $30, 50, 70, 80, 90, 100, 120$ and 140°. On the IAE spectrometer we measured the $Ba_{0.6}K_{0.4}BiO_3$ sample at room temperature [33]. The incident neutron energy was fixed with the help of a beryllium filter and the energy of scattered neutrons was determined by neutron time of flight from sample to detector. The neutron energy gain spectrum was measured for the scattering angles: $15, 30, 45, 60, 75$ and 90°.

In both cases the background from the cryostat with an empty sample can was subtracted and the spectra were summed over the scattering angles to result in rather good averaging over neutron momentum transfer. In the framework of the one phonon approximation one can transform thus averaged time of flight spectra into the generalized phonon density of states [34, see e.g.]:

$$G(\omega) \sim I(t)\exp(2W(Q))\frac{k_i}{k_f}\frac{2M\omega}{1+n(\omega)}\frac{1}{\hbar Q^2 N(\omega)}.$$

Here I(t) is the time of flight spectrum; 2W(Q) the Debay-Waller factor, $n(\omega)$ the Bose-Einstein distribution; $N(\omega)$ the incident neutron spectrum. The results obtained in this way for the $Ba_{0.6}K_{0.4}BiO_3$ compound on two spectrometers at room temperature agree well. Therefore, in the further, we shall discuss only the KDSOG-M spectrometer data as they were obtained also at low temperatures. This will allow us to neglect, in the first approximation, the Debay-Waller factor and avoid the necessity of correction for multiphonon scattering.

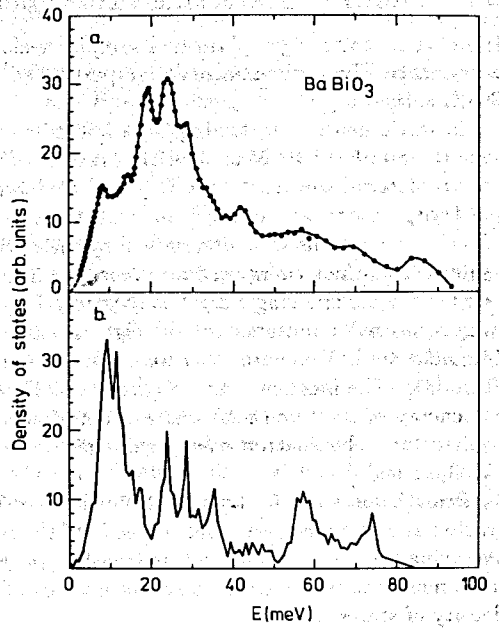
4 Phonon density of states

In order to compare the results obtained in the frame of the above described model with the neutron scattering data we have calculated the phonon density of states:

$$g(\omega) = \sum_j \int dq\delta[\omega - \omega_j(q)].$$

Integration over the Brillouin zone was replaced by summation over 250 points in the $\frac{1}{48}$ of the zone. Strictly speaking, it is the generalized density of states function that should

Fig.2.
Comparison between the calculated phonon density of states (lower curve) and the experimental generalised density of states for $BaBiO_3$.



be brought into comparison with the experimental data to take into account the amplitudes of atomic displacements and the partial contributions to the scattering cross section of different species. This will affect relative intensities of the peaks in the density of states function. If one had taken into account the spectrometer resolution, agreement between calculation and experiment could be still better [36]. We have calculated $g(\omega)$ only, as the simplified model used could hardly be expected to yield results in quantitative agreement with experiment.

The analysis of the experimental data obtained for different temperatures has shown no difference in generalized density of states within experimental errors. The minor difference between these functions, when extracted from the room temperature data, can be attributed to multiphonon effects. The discussion to follow will be, therefore, based on the data obtained at 10K.

Figure 2 presents the data obtained for $BaBiO_3$. The experimental generalized density of states shows peculiarities at 8, 14, 19, 24, 29, 42, 56, 69 and 84 meV and additionally a shoulder is seen at 33 meV. In general, the positions of these peculiarities are in agreement with earlier results [35, 36]. The main difference between our data and those of [35] is in intensity of peaks observed at energies above 35 meV. This can't be due to different spectrometers resolution. Two factors are likely to be the reason for it. First is the different oxygen content of samples used in our experiment and in [35] due to different preparation methods. Second, the different quality of data averaging over neutron momentum transfer and the coherent scattering effects. Figure 2b illustrates the data on the phonon density of states calculated for $BaBiO_3$ in the frame of the above described model. The comparison of calculated with experimental curves shows satisfactory agreement of the data. The model describes two peaks observed below 17 meV. Two strong peaks in the region from 17 to 30 meV are also in agreement with experiment. The librational mode of the BiO_6 octahedron is responsible for the peak observed in experiment at nearly 42 meV and the calculation shows this peak at somewhat lower value of 36 meV. We think the agreement of the theory with experiment can be assumed satisfactory and at higher frequencies as well, because the calculation was done for the cubic symmetry, while the real crystal is monoclinic.

Fig.3.
The same as Fig.2 for $Ba_{0.6}K_{0.4}BiO_3$.

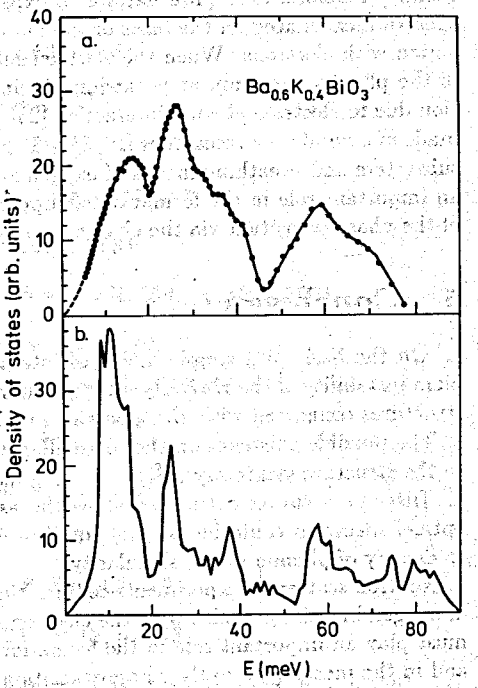


Figure 3a presents the experimental generalized density of states for $Ba_{0.6}K_{0.4}BiO_3$. Similarly to that from earlier experiments [16, 33, 35, 36] this function shows the decrease in number of Van Hove singularities, the shift of the upper boundary towards lower energies in the spectrum and very low density of states between 40 and 50 meV. On

the contrary, in the vicinity of 60 meV the density of states grows in comparison with $BaBiO_3$. Good agreement should be noted for the given system of our experiment and Loong's data [36]. Figure 3b illustrates the calculated phonon density of states. Model calculations show that differently from $BaBiO_3$ doping with potassium leads to the appearance of the only one peak in the density of states in the 20–30 meV region, in good agreement with experiment. Positions of the main Van Hove singularities are in rather good agreement with both the neutron experimental data and the earlier calculations by the molecular dynamics method [35, 36]. At the same time, potassium doping results in a shift of the phonon spectrum boundary towards higher frequencies, while the experiment evidences for the opposite tendency. Analysis of the polarization vectors of the phonon modes shows that at energies above 50 meV the main contribution to the density of states is due to the breathing modes of oxygen atoms vibrations around Ba (or K) atoms. This conclusion agrees with earlier calculations [36]. A potassium atom is lighter than a Ba atom. Therefore, it is quite natural to expect higher frequency modes to appear in the spectrum calculated on the basis of the ion model without taking into account the interaction with electrons. When the electron subsystem is taken into account, the softening of the phonon spectrum at potassium doping can be explained by phonon renormalization due to electron–phonon interaction [23]. Thus, our results agree with the conclusion, made in a number of researches [16, 35, 36], about strong interaction between the electron subsystem and breathing modes of oxygen atoms . This interaction is most likely to play an important role in the formation of superconducting properties and in the mechanism of the phase transition via the charge density wave [7].

5 Conclusions

1. On the basis of a simple model of interatomic potential it appeared possible to explain instability of the $BaBiO_3$ cubic phase with respect to transitions to lower symmetry structures connected with BiO_6 octahedral tilt.
2. The possible existence on the phase diagram was predicted for a region corresponding to the structure symmetry $R\bar{3}c$.
3. Dispersion curves calculated allow the assumption that the peak at 40 meV in the optical spectrum could be due not to vibrations in the center of the Brillouin zone, but to density of phonon states singularity.
4. Neutron scattering experiments confirm the earlier conclusion about strong interaction of oxygen breathing modes with the electron subsystem. We believe that this interaction must play an important role in the formation of superconducting properties of a system and in the mechanism of the phase transition via the charge density wave formation.
5. The calculated density of phonon states provides a good description of the experimental data and is in good agreement with the data obtained by the molecular dynamics method.

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