Synthesis of $Ba_{1-x}K_xBiO_3$ ceramic specimens:
Electron paramagnetic resonance and microwave absorption

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$Ba_{1-x}K_xBiO_3$ ceramic samples were synthesized with many initial relative amounts of reagents. Chemical analysis was used to determine the final concentration $\bar{x}$ in the synthesized samples. It was found that only four values of $\bar{x}=0.13, 0.25, 0.4, 0.5$ with $\Delta\bar{x}=\pm0.03$ were possible. Electron-paramagnetic resonance (EPR) and microwave-absorption investigations of the synthesized ceramic specimens were carried out in the temperature range 4–100 K. In the two nonsuperconducting specimens characterized by the smaller concentrations $\bar{x}=0.13, 0.25$ the same two EPR lines at $g=2.09$ and $g=4.25$ were observed, whose intensities increased sharply below 40 K with decreasing temperature, likely due to the phase $Ba_{0.875}K_{0.125}BiO_3$. A least-squares fitting of the intensity of the line at $g=4.25$ for the sample with $\bar{x}=0.13$ with $(1/T)\exp(-J_p/T)$, yielded the value of the exchange constant $J_p=2.3\pm0.5$ K, confirming that this line is indeed due to a transition within the energy levels belonging to the excited triplet state of hole pairs localized on the oxygen ions. Low-field microwave absorption and x-ray diffraction by the superconducting specimens characterized by the higher concentrations $\bar{x}=0.4, 0.5$ indicate that these samples consist of two different superconducting phases: one, with $x=0.375$, possessing $T_c=28$ K, and the other with $x=0.5$, possessing $T_c=16$ K. Four possible configurations of the solid solutions $Ba_{1-x}K_xBiO_3$ wherein one, two, three, and four K^+ ions substitute for the same number of Ba^{2+} ions, with well-defined positions of K^+ ions in the unit cell, have been presently proposed.

I. INTRODUCTION

Since the discovery of high-T_c superconductivity many theoretical models have been proposed to explain this phenomenon, but none has proven itself to be completely satisfactory. It is of great interest to know whether superconductivity is due to paired charge carriers, or due to condensation of bosons consisting of stable, bound pairs. Such localized pairs can be conveniently studied by electron-paramagnetic resonance (EPR).

K^+ doping of $BaBiO_3$ to produce $Ba_{1-x}K_xBiO_3$ by substituting K^+ for Ba^{2+} ions introduces holes in the oxygen $2p$ levels for charge compensation, which serve as charge carriers. The symmetry of these compounds changes with concentration of K^+ ions at temperatures below 100 K from monoclinic ($P2/m$) for $x=0$, to monoclinic ($I2/m$) for $0<x<0.1$, to orthorombic ($Ibmm$) for $0.1<x<0.35$, and to cubic ($Pm\bar{3}m$) for $x>0.35$, following the phase diagram of Pei *et al.*[1] The structural transition that occurs when the concentration of K^+ ions is increased above $x=0.375$ is known as Peierls transition.[2] The highest temperature at which transition to superconductivity take place ($T_c\cong30$ K) in this system is that of the compound with $x=0.4$ as determined from measurement of conductivity.[1] Further increase in K content leads to a decrease in T_c, e.g., that of the compound with $x=0.5$ is about 15 K.[1] First determination of T_c in multiphase $Ba_{1-x}K_xBiO_3$ samples yielded T_c values between 15 to 22 K as determined by Mattheiss from magnetic-susceptibility measurements.[3] The value of the gap width was estimated from tunnel-junction conductance behavior[4] (dI/dV curve) to be $\Delta=1.375\,kT_c$ ($T_c=30$ K) for the com-

pound with $x=0.4$. In addition, the value of the parameter $\alpha=0.43\pm0.03$ (Ref. 5) that represents the O^{17}-isotope effect for this material was greater than 0.3 indicating that it was a conventional (BCS) superconductor rather than that characterized by an unconventional pairing mechanism. However, further investigations confirming the change of the sign of thermoelectric emf near the phase transition temperature T_c,[6] and the deviation of the temperature dependence of the resistivity from that for the hopping resistivity at low temperatures[7,8] indicated that the mechanism of superconductivity in $Ba_{1-x}K_xBiO_3$ was rather complex, being more like that effective in oxide superconductors, e.g., $La_{2-x}Sr_xCuO_4$, wherein localized hole pairs have been observed by EPR by Thomann *et al.*,[9] who discussed various possibilities of formation of hole pairs in $La_{2-x}Sr_xCuO_4$, either on an oxygen ion or on a copper ion. They concluded that in $La_{2-x}Sr_xCuO_4$, most likely, a hole pair is constituted by two nearest holes on oxygen ions, interacting with the copper ion, causing ferromagnetic alignment of oxygen holes.

In the present paper, EPR/microwave-absorption measurements on four synthesized diamagnetic oxide superconducting materials $Ba_{1-x}K_xBiO_3$, without copper, characterized by the final concentrations $\bar{x}=0.13, 0.25, 0.4, 0.5$ are presented. The absence of Cu^{2+} ions provides a convenience in that all effects due to $3d$-electron magnetism are absent here. In particular, (i) the nature of the paramagnetic centers responsible for EPR signals in the samples with $\bar{x}=0.13, 0.25$, and (ii) existence of different superconducting phases in the samples $\bar{x}=0.4, 0.5$ have been investigated. Further, the possible structural configurations of $Ba_{1-x}K_xBiO_3$ have been

proposed. No EPR studies have so far been reported on these samples. Preliminary microwave-absorption studies of Ba$_{1-x}$K$_x$BiO$_3$ ceramic specimens irradiated by x-ray and low-energy electrons have been reported by Kärner *et al.*[10]

II. SYNTHESIS AND STRUCTURE OF Ba$_{1-x}$K$_x$BiO$_3$

All the ceramic specimens of Ba$_{1-x}$K$_x$BiO$_3$ were grown following the usual two-stage technique.[5] (Hereafter, $\bar{x}$ and x represent, respectively, the chemically determined amount of K$^+$ ions in synthesized samples, and in the chemical phases Ba$_{1-x}$K$_x$BiO$_3$.) In the first stage, the reagents Ba(OH)$_2$, KOH, Bi$_2$O$_3$ or Ba(NO$_3$)$_2$, KNO$_3$, Bi$_2$O$_3$ were mixed together. The mixture was then ground and heated at temperatures from 948 to 1123 K during intervals of 12–24 h. In the second stage, the specimens were annealed in an oxygen atmosphere in the temperature range 723–748 K for 1 h. This technique yielded the nonsuperconducting specimens with the final concentration $\bar{x}=0.13$ and $\bar{x}=0.25$, and the superconducting specimens with the final concentration $\bar{x}=0.4$ when a large excess of KOH content over and above that required for the stoichiometric composition was used. The synthesis of the samples with higher concentration of K$^+$ ions ($\bar{x}=0.5$) involved stepped heating from 673 to 1123 K, increasing the temperature by 323 K every 2 h, followed by annealing in an oxygen atmosphere at 723 K. Numerous attempts with different starting mixtures yielded only four compositions characterized by the K content, $\bar{x}=0.13$, 0.25, 0.4, 0.5 with $\Delta\bar{x}=\pm0.03$, as determined by chemical analysis, similar to that reported by Anshukova *et al.*[11] It is noted that the value of $\bar{x}$, as determined by chemical analysis, describes the presence of K$^+$ ions relative to Ba^{2+} ions and not really the different phases, which can only be determined, for examples, by x-ray, EPR, and microwave-absorption experiments.

The valence of bismuth ions in the noncubic compounds BaBiO$_3$ and Ba$_{1-x}$K$_x$BiO$_3$ ($x<0.375$) has not been unequivocally understood so far. Different Bi(1)-O and Bi(2)-O distances suggest a difference in the charge density of the two inequivalent sites for Bi ions in the unit cell, leading to the formula BaBi$_{0.5}^{3+}$Bi$_{0.5}^{5+}$O$_3$.[12] However, theoretical calculations[13] indicate that the charge density contours surrounding Bi(1) and Bi(2) sites are almost identical in accordance with those determined by photoelectron spectroscopy data.[14] Transmission-electron microscopy and selected-area-diffraction data reported by Pei *et al.*[15] confirmed the existence of commensurate as well as incommensurate charge-density waves in the nonsuperconducting phases of these compounds. Charge disproportionation in these compounds suggests, in accordance with Anshukova *et al.*,[16] that there exist holes on the oxygen ions, which are paired, as well as ordered along the c axis, described by the formula Ba$_2$Bi$_2^{3+}$O^{0}O$_5^{2-}$. Both Ba$_2$Bi$_2^{3+}$O^{0}O$_5^{2-}$ and BaBi$_{0.5}^{3+}$Bi$_{0.5}^{5+}$O$_3$ describe, in fact, extreme situations, since Bi-O hybridization of the $2p$ levels of the oxygen ion and that of the $6s$ and $6p$ levels of the Bi ion leads to chemically stable valences of the bismuth ion as Bi^{3+} and Bi^{5+} in these compounds. In reality, the BiO$_6$ polyhedra that exist in these compounds, are characterized by the values of the valence of the bismuth ion anywhere between +3 and +5.[12]
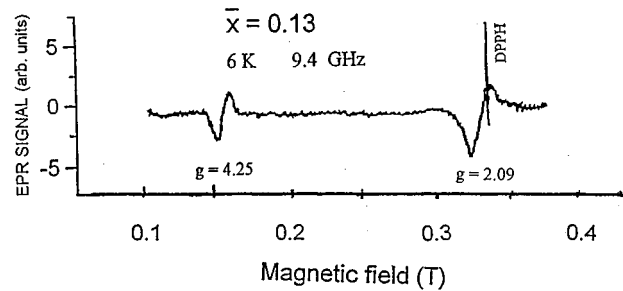

FIG. 1. *X*-band (9.4 GHz) EPR spectrum of the ceramic sample with $\bar{x}=0.13$ at 6 K.

III. EXPERIMENTAL ARRANGEMENT, EPR DATA AND MICROWAVE-ABSORPTION MEASUREMENTS

EPR experiments were carried out at *X* band (9.4 GHz) on an RE-1306 spectrometer in the temperature range 4–300 K using a helium gas-flow cryostat. For temperature control (stability ±0.5 K) and its measurement, a 0.02 mm Cromel-Au$_{Fe}$ thermocouple was used. In order to measure microwave absorption at near-zero magnetic fields in the superconducting samples, two Helmholtz coils were mounted on the magnet poles, which produced a stable magnetic field (up to 20 mT) in the direction opposite to that of the magnetic field produced by the spectrometer magnet.

Nonsuperconducting specimens ($\bar{x}=0.13$, 25): EPR signals. The specimen of pure BaBiO$_3$ did not exhibit any EPR signal. On the other hand, in each of the ceramic polycrystalline specimens, with $\bar{x}=0.13$, 0.25 two broad EPR lines were observed below 40 K situated at $g=2.09$ and $g=4.25$, as exhibited in Fig. 1 for the sample with $\bar{x}=0.13$ at 6 K. The intensity of these signals depended on the particular thermal treatment and annealing in oxygen atmosphere to which a samples was subjected. The intensity of these signals decreased with time that elapsed after synthesis. Their intensities (peak-to-peak heights) increased sharply with decreasing temperature in the same fashion. The temperature variation of the EPR line situated at $g=4.25$ for the sample with $\bar{x}=0.13$ in the temperature interval 6–38 K is shown in Fig. 2, while Fig. 3 exhibits the temperature dependence of the intensity of this line. The intensity of the EPR signals, connected with the transitions between the levels of the excited triplet state due to a hole pair depends on temperature approximately as $I\sim(1/T)\exp(-J_p/T)$, where T is the temperature.[17] This implies a maximum in the intensity at a temperature characteristic of the exchange constant J_p. No maximum was observed in the present case because measurements were not carried out below 6 K. Least-squares fitting of this expression to the experimental EPR line intensity of the line at $g=4.25$ for the sample with $\bar{x}=0.13$ (Fig. 3) yielded an antiferromagnetic value of the exchange constant of the hole pair $J_p=2.3\pm0.5$ K. The width of this line was temperature independent, being 12 mT. The observed EPR lines were not due to a transition-metal ion, e.g., Fe^{3+}, since they were observed in all the samples, although prepared with different initial reagents (hydrates and nitrates) and impurities. Further, the temperature dependence of such signals is too sharp to be due to the Fe^{3+} ion.[9]

These EPR signals are, in fact, due to hole pairs localized on the oxygen ions characterized by the exchange interaction

$\bar{x} = 0.13$

6 K
8 K
10 K
12 K
18 K
20 K
24 K
28 K
32 K
38 K

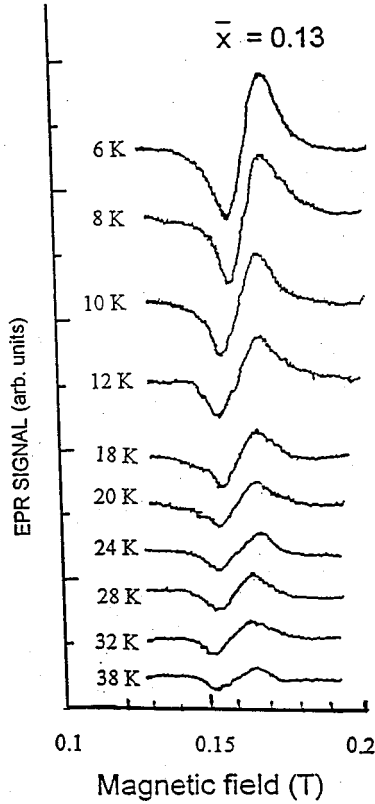0.1   0.15   0.2

Magnetic field (T)

FIG. 2. Temperature variation of X-band (9.4 GHz) EPR signal at $g=4.25$ for the ceramic sample with $\bar{x}=0.13$ in temperature interval 6–38 K. (Although the shape of the signal appears to be similar to that in Figs. 5 and 6, the latter are due to microwave absorption about zero external field rather than being EPR signals.)

$J_p \mathbf{S}_{h1} \cdot \mathbf{S}_{h2}$, where $S_{h1}=S_{h2}=\frac{1}{2}$ are the spins of the two holes. The energy levels for such a pair can be described by the spin Hamiltonian $\mathbf{S}_i=\mathbf{S}_{h1}+\mathbf{S}_{h2}$, with S_i describing the total
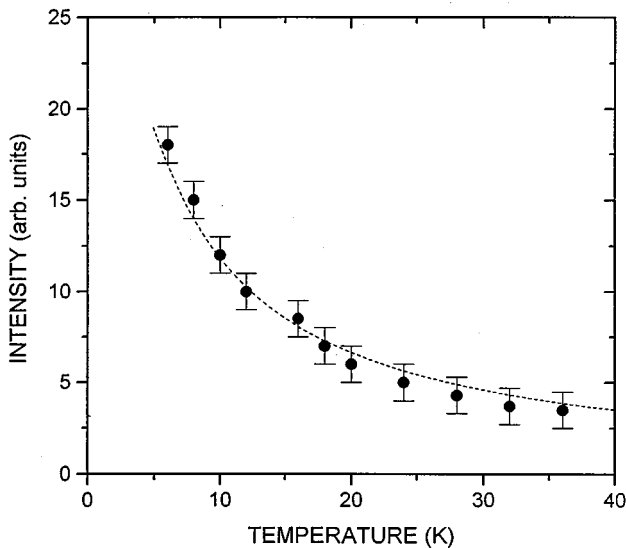
FIG. 3. Temperature dependence of the intensity (peak-to-peak height) of the EPR signal at $g=4.25$ for the ceramic samples with $\bar{x}=0.13$. The circles represent experimental data while the dashed line indicate the results of least-squares fitting to $(1/T)\exp(-J_p/T)$, which yields $J_p=2.3$ K.
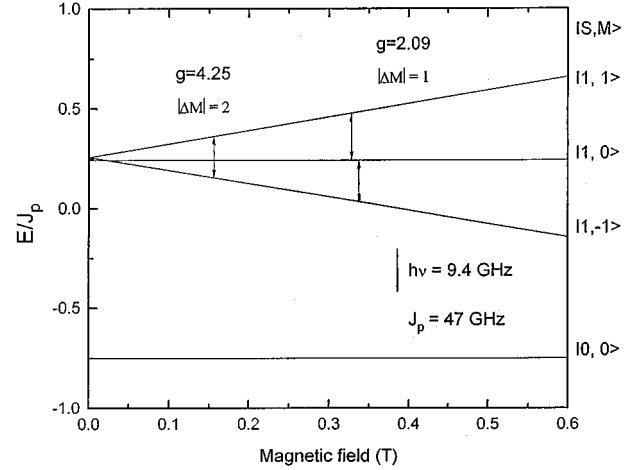
FIG. 4. The energy levels of a hole pair as a function of the external magnetic field intensity, described by the spin Hamiltonian given by Eq. (1), in the unit of the presently-estimated value of $J_p(=47\text{ GHz}=2.3\text{ K})$. An isotropic $g=2$ has been assumed. A small zero-field splitting due to crystal field, Δ, has been shown. (According to present data $\Delta\cong0$, since the EPR lines due to transition $+1\leftrightarrow0$ and $0\leftrightarrow-1$ with the Zeeman levels of the triplet are not resolved.)

spin of the pair with two possibilities ($S_1=0$, $S_2=1$):

$$H=\mu_B \mathbf{g}_i \mathbf{B}\cdot\mathbf{S}+J_p[S_i(S_i+1)/2-3/4]; \quad (i=1,2). \quad (1)$$

In Eq. (1), μ_B is Bohr magneton, the subscript $i=1,2$ describes the singlet (nonmagnetic: $g_1=0$, $S_1=0$) and the triplet (magnetic: $g_2\neq0$, $S_2=1$) states, respectively. (Hereafter, g,S refer to the excited triplet state.) For the antiferromagnetically coupled hole pair ($J_p>0$) the ground state is a singlet and the excited state is a triplet, as shown in Fig. 4. The EPR spectra can be observed when the triplet is thermally populated. The presently observed EPR line at $g=2.09$ is an overlap of the allowed transitions $M=+1\leftrightarrow0$ and $-1\leftrightarrow0$ (M is the electronic quantum number of the triplet state), occurring at about the same magnetic field value for an isotropic g and negligible zero-field splitting of the triplet levels. The so-called "half-field" signal with $g=4.25$ associated with the "forbidden" transition $M=-1\leftrightarrow+1$ is typical of a triplet center.[17] In some specimens, additional verynarrow signals due to the "two quantum" $-1\leftrightarrow0\leftrightarrow+1$ transitions[17] (peak-to-peak first derivative linewidth $\Delta H_{pp}=0.4$ mT) at $g=2.05$, were also observed. The fact that the same EPR lines were observed in both the samples with $\bar{x}=0.13$ and $\bar{x}=0.25$ implies that they both contain the same paramagnetic phase responsible for the EPR signal.

The fact that the sample of pure $BaBiO_3$ does not exhibit any EPR signal, leads to the conclusion that localized hole pairs appear only as a consequence of K doping of $BaBiO_3$. The present experimental data do not enable one to distinguish between the two possibilities of hole-pair formation: (i) Pairing of holes on two different closest oxygen ions, similar to that proposed by Thomann et al.;[9] (ii) formation of hole pairs only on the same oxygen ion.

Superconducting samples ($\bar{x}=0.4$, 0.5): microwave absorption. For observation of low-field absorption the following procedure was used. The magnetic field was maintained
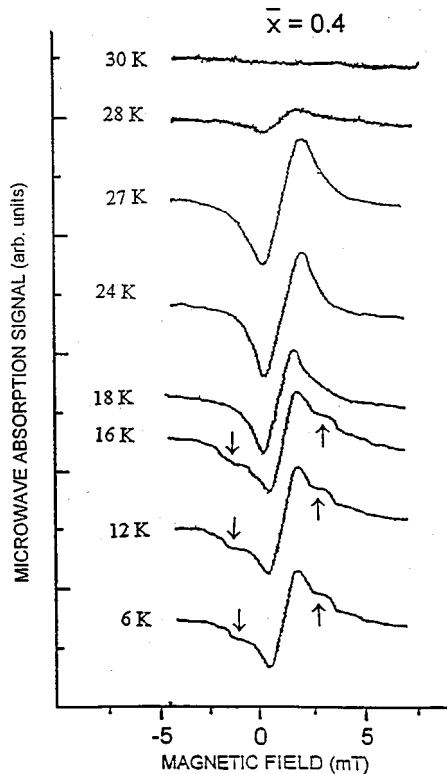
FIG. 5. Temperature variation of the low-field microwave-absorption signal in the sample with $\bar{x}=0.4$ in the interval 6–30 K. The arrows indicate the wings of X band (9.4 GHz), which represent the signal due to the phase with $T_c=16$ K. (Despite similar appearance, this plot is different from that of Fig. 2; the latter exhibits an EPR signal and not microwave absorption.)
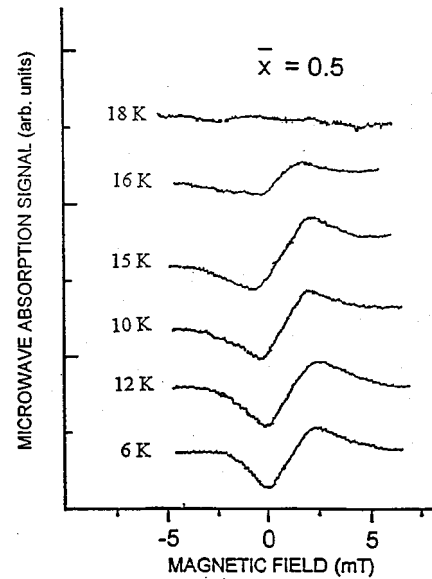

FIG. 6. Temperature variation of the low-field X band (9.4 GHz) microwave-absorption signal in the sample with $\bar{x}=0.5$ in the interval 6–18 K. (Despite similar appearance, this plot is different from that of Fig. 2; the latter exhibits an EPR signal and not microwave absorption.)

at zero during initial cooling. It was thereafter increased gradually to 5 mT to record the microwave absorption as a function of field. The hysteresis of the signals of microwave absorption for the specimens with $\bar{x}=0.4$ did not exceed 0.1 mT in these experiments. The microwave low-field absorption signals for samples with the compositions $\bar{x}=0.4$ (between 6 and 30 K) and $\bar{x}=0.5$ (between 6 and 16 K) are shown in Figs. 5 and 6, respectively. In Fig. 5, the wings on the left and right sides of the main absorption signal, indicating overlap by another absorption signal, disappear above 16 K. However, the main part of the signal disappears only above 28 K, implying that this sample consists of two different superconducting phases $Ba_{0.625}K_{0.375}BiO_3$ and $Ba_{0.5}K_{0.5}BiO_3$, whose T_c values are known to be 28 and 16 K, respectively.[1,11] The phase transitions occurred within a narrow temperature interval of only 1 K, while the hysteresis in T_c, as measured when the temperature was increased and decreased, did not exceed 2 K. As seen from Fig. 6, low-field microwave absorption in the sample with $\bar{x}=0.5$ disappeared above 16 K, the same as that exhibited by the sample with $\bar{x}=0.4$ with $T_c=16$ K, indicating that this sample consists of only one superconducting phase ($Ba_{0.5}K_{0.5}BiO_3$). Further, in this sample the phase transition occurred in a very narrow temperature interval of 2 K, the hysteresis of phase transition being of the same order as that in the sample with $\bar{x}=0.4$. It is thus concluded that there exist only two superconducting $Ba_{1-x}K_xBiO_3$ phases, which are characterized by $x=0.375$

and $x=0.5$. Affronte et al.[18] suggested the existence of two superconducting phases, one with $T_c=30$ K (with $x=0.35$) and second with $T_c=25$ K (with $x=0.45$), and the existence of a third phase with $x=0.5$, and $T_c=15$ K. No evidence of the existence of the phases with $T_c=25$ K and $T_c=30$ K is available in the presently reported data. The 295 K x-ray-diffraction pattern of the samples with $\bar{x}=0.4$, 0.5 also consist of two sets (1 and 2) of diffraction peaks with larger proportion of peaks corresponding to sets 1 and 2 in the samples with $\bar{x}=0.4$ and $\bar{x}=0.5$, respectively, as exhibited in Fig. 7, confirming the coexistence of the compositions $Ba_{0.625}K_{0.375}BiO_3$ and $Ba_{0.5}K_{0.5}BiO_3$. The x-ray diffraction peaks for the sample with $\bar{x}=0.4$ do correspond to those reported by Fleming et al.[19]

Superconducting samples ($\bar{x}=0.4, 0.5$): EPR signal above T_c. In the specimens with $\bar{x}=0.4$ and $\bar{x}=0.5$ no EPR signals at $g=4.25$ were observed in the normal state above their respective T_c. Only in the sample with $\bar{x}=0.4$ one very weak broad EPR line at $g=2.05$, ascribed also to localized hole pairs, was observed in the temperature range 4–15 K, whose intensity increased as the temperature was decreased exhibiting a broad maximum around 5 K. This line is then due to transition within the triplet state characterized by a larger J_p value than that for the sample $\bar{x}=0.13$ so that the maximum of the intensity was observed at 5 K, unlike that for the sample with $\bar{x}=0.13$, for which, as discussed above, the maximum in the intensity lies below 6 K, which is not observed as the measurements were only carried out to 6 K (Fig. 3). This line then is interpreted to be due to the presence of the same paramagnetic phase that exists in the samples with $\bar{x}=0.13$ and $\bar{x}=0.25$.

IV. POSSIBLE CONFIGURATIONS FOR $Ba_{1-x}K_xBiO_3$ SOLID SOLUTIONS

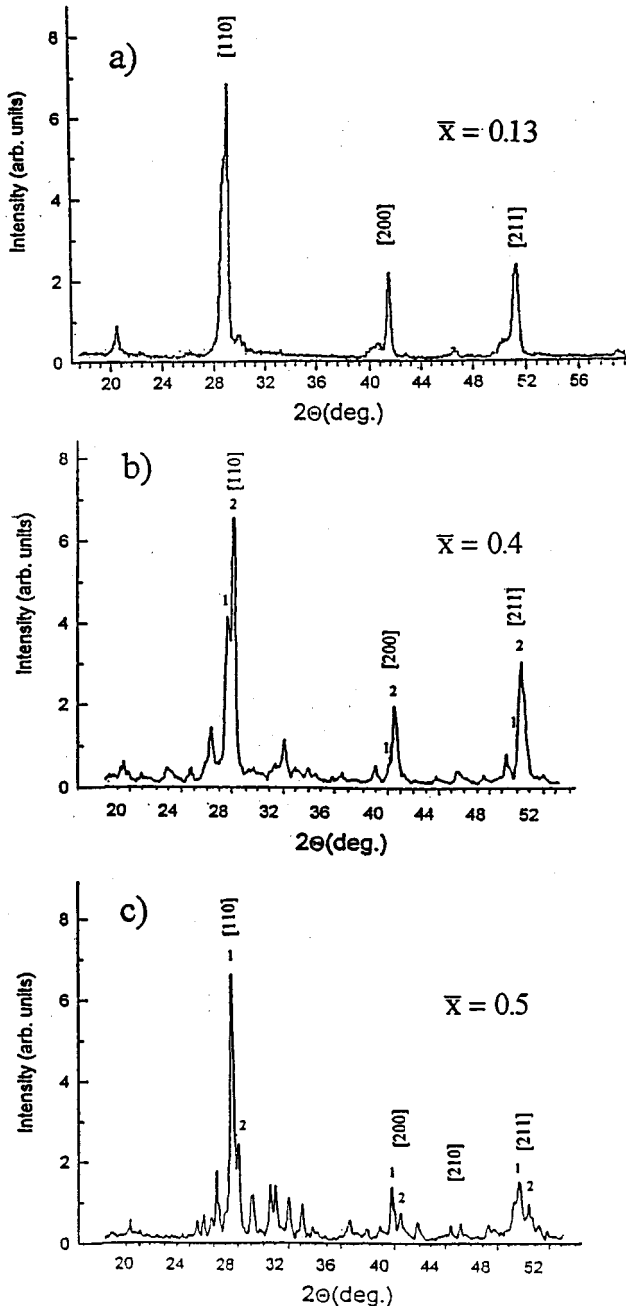It is proposed here, on the basis of the present experimental data, that there exist only four configurations in

FIG. 7. X-ray-diffraction peaks for $Ba_{1-x}K_xBiO_3$ specimens at $T=295$ K: (a) $\bar{x}=0.125$; (b) $\bar{x}=0.4$; (c) $\bar{x}=0.5$. In (b) and (c) the peaks labeled as 1 correspond to $Ba_{0.5}K_{0.5}BiO_3$, while the peaks labeled as 2 to $Ba_{0.625}K_{0.375}BiO_3$. The diffraction patterns corresponding to $Ba_{0.625}K_{0.375}BiO_3$ are the same as those reported for $Ba_{0.6}K_{0.4}BiO_3$ by Fleming et al. (Ref. 19).

$Ba_{1-x}K_xBiO_3$ wherein one, two, three, or four Ba^{2+} ions have been substituted for by the same number of K^+ ions in the unit cell as exhibited in Fig. 8. That proposed for $x=0.5$ is in accordance with the configuration for the $Ba_{0.5}K_{0.5}BiO_3$ ordered alloy, wherein exist alternate planes of K^+ and Ba^{2+} ions perpendicular to the [111] diagonal, possessing the so-called rocksalt structure. The first suggestion of such ordering of K^+ ions was made by Mattheiss et al.[13] in context with the electron structure of such ordered alloys. Accordingly, hole pairs are created in $Ba_{1-x}K_xBiO_3$ on the oxygen
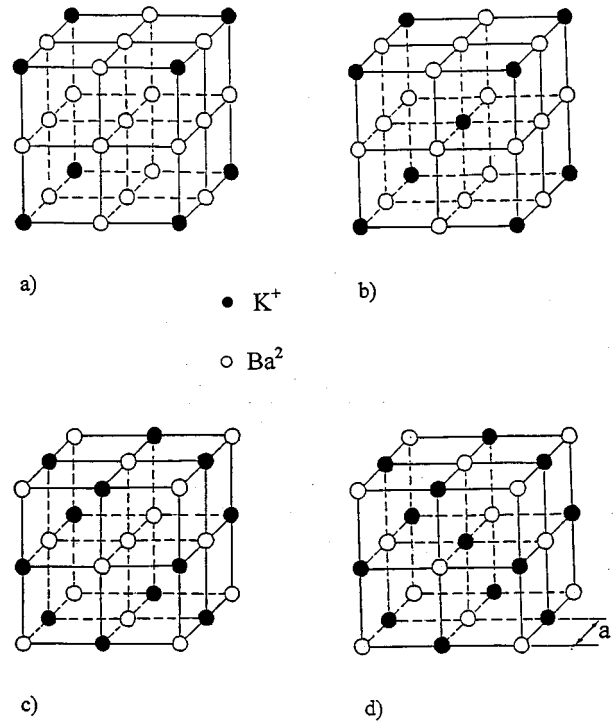

FIG. 8. The proposed orderings of K^+ ions in the $Ba_{1-x}K_xBiO_3$ structure for samples with different compositions: (a) one K^+ ion replacing one Ba^{2+} ion; (b) two K^+ ions replacing two Ba^{2+} ions; (c) three K^+ ions replacing three Ba^{2+} ions; (d) four K^+ ions replacing four Ba^{2+} ions. Only Ba^{2+} and K^+ ions are shown. The solid and open circles represent K^+ and Ba^{2+} ions, respectively.

ions to compensate for the charge difference in the valence states of Bi^{2+} and K^+ ions. In the compounds presently investigated, the compensation of extra charge by deficiency of oxygen ions does not occur, because the second stage of the synthesis involved annealing in oxygen atmosphere.

In light of the same EPR lines being observed in the various samples ($\bar{x}=0.13$, 0.25, 0.4) it appears that the samples with $\bar{x}=0.13$, 0.25 consist of the phase $Ba_{0.87}K_{0.125}BiO_3$ in which one K^+ ion replaces one Ba^{2+} ion, since this is the only possible phase consistent with the chemically determined K^+ content in the sample with $\bar{x}=0.13$. On the other hand, the present microwave-absorption data, in conjunction with x-ray-diffraction spectra, indicate that both of the samples with $\bar{x}=0.4$, 0.5 contain the two phases wherein three ($Ba_{0.625}K_{0.375}BiO_3$) and four ($Ba_{0.5}K_{0.5}BiO_3$) Ba^{2+} ions have been replaced by three and four K^+ ions, respectively. In addition, the sample with $\bar{x}=0.4$ also contains the phase $Ba_{0.875}K_{0.125}BiO_3$ responsible for the EPR signal at low temperature.

V. CONCLUDING REMARKS

The main features of the present study are (i) The EPR and microwave-absorption study reported in this paper clearly indicates the existence of localized hole pairs in $Ba_{1-x}K_xBiO_3$ samples, which play an important role in the mechanism of superconductivity.

(ii) Three different phases have been detected. One of these ($Ba_{0.875}K_{0.125}BiO_3$) is responsible for the EPR lines in

the samples with $\bar{x}=0.13$, $\bar{x}=0.25$ as well as in the sample with $\bar{x}=0.4$ (on the surface). While the other two are superconducting with $T_c=28$ K ($Ba_{0.625}K_{0.375}BiO_3$) and $T_c=16$ K ($Ba_{0.5}K_{0.5}BiO_3$), respectively.

(iii) Four possible configurations of the solid solutions $Ba_{1-x}K_xBiO_3$ have been proposed, characterized by $x=0.125$, 0.25, 0.375, 0.5 with one, two, three, and four Ba^{2+} ions, being substituted for K^+ ions, respectively. It is suggested that the EPR spectra are due to the phase $Ba_{0.875}K_{0.125}BiO_3$ wherein one Ba^{2+} ion has been replaced by one K^+ ion, while the two superconducting phases corre-

spond to the structures $Ba_{0.625}K_{0.375}BiO_3$ and $Ba_{0.5}K_{0.5}BiO_3$ in which 3 and 4 K^+ ions substitute for 3 and 4 Ba^{2+} ions, respectively. It is hoped that further experimental data will put the proposed configurations of the solid solutions $Ba_{1-x}K_xBiO_3$ on better footing.

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