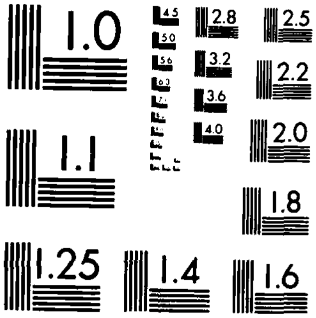
AD-A143 556 STUDIES OF STRUCTURAL PROPERTIES AND THEIR RELATIONSHIP 1/1
TO CRITICAL PARAM..(U) NORTHERN ILLINOIS UNIV DE KALB
DEPT OF PHYSICS C W KIMBALL 28 FEB 84 82-219
UNCLASSIFIED AFOSR-TR-84-0550 AFOSR-80-0010 F/G 20/3 NL

END
FILMED
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A143 556

DTIC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

(1.2)

1. REPORT NUMBER
AFOSR-TR- 84-0550

2. GOVT ACCESSION NO.
AD-A143 556

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Studies of Structural Properties and their Relationship to Critical Parameters in Superconducting Materials

5. TYPE OF REPORT & PERIOD COVERED
FINAL 10/1/79 - 12/31/83

6. PERFORMING ORG. REPORT NUMBER
82-219

7. AUTHOR(s)
C. W. Kimball

8. CONTRACT OR GRANT NUMBER(s)
AFOSR 80-0010

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Board of Regents for
Northern Illinois University
DeKalb, IL 60115

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
61102F
2305/B1

11. CONTROLLING OFFICE NAME AND ADDRESS
AFOSR/NE
Bolling Air Force Base Washington, D. C. 20332

12. REPORT DATE
2/28/84

13. NUMBER OF PAGES
31

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
--

15. SECURITY CLASS. (of this report)
unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
--

Approved for public release;
distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
--

18. SUPPLEMENTARY NOTES
--

JUL 30 1984

A

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Superconducting Materials, Mossbauer effect
Superconducting Oxides
Perovskites
Conversion Electron Mossbauer Spectroscopy

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The project sponsored by the Air Force Office of Scientific Research (AFOSR 80-0010) comprised an experimental study of the electronic and vibrational properties of superconducting materials by means of Mossbauer spectroscopy. From the temperature dependence of the Mossbauer parameters of tin in the oxide superconductor $\mathrm{Ba(Pb_{0.67}Sn_{0.03})Bi_{0.3}O_3}$, phonon softening, characteristic of displacive transitions, was found to take place above the superconducting transition temperature. This observation is hence (over)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

84 07 24 024

Abstract (continued) Block 20

important for understanding the superconducting properties of those perovskite compounds. The Mossbauer effect at ^{121}Sb in $BaPb_{1-x}(Bi,Sb)_xO_3$ shows that Sb is 5+. The range of stability of the perovskite compounds was determined in the ternary systems $Ba(Pb\text{-}Sn\text{-}Bi)O_3$ and $Ba(Pb\text{-}Sb\text{-}Bi)O_3$. The composition dependence of the superconducting transition temperature was determined for both ternary systems. Conversion Electron Mossbauer Spectroscopy has been applied to the study of Nb_3Sn superconducting films. This tool has been found to provide a unique probe of the electronic and vibrational properties of thin film materials.

A-1

STUDIES OF STRUCTURAL PROPERTIES AND THEIR RELATIONSHIP TO CRITICAL PARAMETERS IN SUPERCONDUCTING MATERIALS

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
GRANT NUMBER 80-0010

FINAL REPORT

February 15, 1984

Clyde W. Kimball

Department of Physics
Northern Illinois University
DeKalb, Illinois 60115
815/753-1773

ABSTRACT

The project sponsored by the Air Force Office of Scientific Research (AFOSR ~~80-0010)~~ comprised an experimental study of the electronic and vibrational properties of superconducting materials by means of Mossbauer spectroscopy. From the temperature dependence of the Mossbauer parameters of tin in the oxide superconductor $Ba(Pb_{0.67}Sn_{0.03})Bi_{0.3}O_3$, phonon softening, characteristic of displacive transitions, was found to take place above the superconducting transition temperature. This observation is hence important for understanding the superconducting properties of the perovskite compounds. The Mossbauer effect at ^{121}Sb in $BaPb_{1-x}(Bi,Sb)_xO_3$ shows that Sb is 5+. The range of stability of the perovskite compounds was determined in the ternary systems $Ba(Pb-Sn-Bi)O_3$ and $Ba(Pb-Sb-Bi)O_3$. The composition dependence of the superconducting transition temperature was determined for both ternary systems. Conversion Electron Mossbauer Spectroscopy has been applied to the study of Nb_3Sn superconducting films. This tool has been found to provide a unique probe of the electronic and vibrational properties of thin film materials.

TABLE OF CONTENTS

The discovery of a high temperature superconducting material ($\sim$ 100 K) with reasonable critical field characteristics would lead to revolutionary changes in many technologies, e.g., electronics and transportation. Although theoretical considerations have led to predictions of limitations ranging from $\sim$ 45 K (electron-phonon) to 100-200 K (exciton), the highest transition temperature so far observed is 23.2 K in Nb_3Ge. This value was achieved only after extensive studies of the technologies of preparation. A relatively small extension of this value to say $\sim$ 30 K would permit easy use of the less expensive liquid-hydrogen technology, rather than the current expensive liquid-helium technology. Several recent discoveries appear to open new paths for experimental exploration: (1) the relatively high transition temperatures in oxide materials, (2) the application of Conversion Electron Mossbauer Spectroscopy to measurement of the lattice vibrational properties of thin film materials, and (3) the apparent enhancement of superconducting properties of eutectics over those of the individual constituents. The basic physical and chemical interactions responsible for these behaviors are in the process of being clarified. This study sponsored by AFOSR has provided information on the chemical bond and the lattice and structural behavior, together with compositional relationships to superconducting properties for (1) and (2) above. The results have extended the base of knowledge necessary for further theoretical treatment and will help to lay a foundation for the development of new paths to better superconducting materials.

The project sponsored by AFOSR Grant 80-0010 comprised an experimental study of the electronic and vibrational properties of superconducting materials by means of Mossbauer spectroscopy. Mossbauer effect measurements elucidate behavior important for determination of the superconducting transition temperatures (T_c). The Mossbauer thermal shift and intensity reflect lattice softening, vibrational anharmonicity and lattice anisotropy.[2] Within the McMillan approximation for strong-coupling, the Mossbauer effect yields measures of the phonon moments important for the phonon-only part of the electron-phonon coupling and, hence, the phonon-only effect on T_c. The centroid of the Mossbauer absorption pattern at high temperature ($T > \theta_D$) is determined by the valence electron structure of the probe atom, and the temperature dependence of the centroid is related to the thermal energy of the solid, e.g., to the Debye temperature in a harmonic system.

OXIDE SUPERCONDUCTORS

The occurrence of high temperature superconducting transitions in oxide compounds has currently motivated high interest in these materials. Several features of their behavior make these materials of special interest; namely, that superconductivity occurs over a composition range between a conducting (M) and semiconducting (S) phase and that the transition temperature reaches a maximum near the M-S boundary, and drops precipitously at the semiconducting phase. Thus, the possibility of interactions other than electron-phonon (BCS) being responsible for superconductivity in the oxides has been raised. For example, a few of the alternate mechanisms are metal-semiconductor interface superconductivity through the excitonic mechanism, or plasmon superconductivity through the interaction of electrons and the electron-hole plasma. Although the understanding of the behavior of this material is incomplete, the intrinsically higher maximum transition temperature for, e.g., excitonic superconductivity ($\sim$ 200 K) compared to that for the electron-phonon interaction ($\sim$ 40 K) clearly makes exploration of these new superconductors important. In addition, even in the few oxide superconductors discovered to date the transition temperatures extend to $\sim$ 15 K, opening vistas for exploration of new superconducting materials.

Johnston et al[3] discovered the first high temperature superconducting oxide, the spinel $Li_{\sim 1}Ti_{\sim 2}O_4$ ($T_c \sim 13.7$ K). This compound was synthesized following the analog of the sulphide $Li_xTi_{2.2}S_2$ ($0.1 < x \leq 0.3$) with T_c ranging from 10 to 15 K.[4] The reason for the occurrence of superconductivity in the oxide spinel is not clear. The superconducting spinel composition is in the region of a composition-induced metal-semiconductor transition. Sleight et al[6] have found the perovskite $BaPb_{1-x}Bi_xO_3$ ($x \cong 0.05$ to 0.3) to be superconducting with transition temperatures to 13 K. This value is very high for a compound which does not contain a transition element. A complete solid solution exists between metallic $BaPbO_3$ and semiconducting $BaBiO_3$. The critical temperature varies from $T_c \cong 9$ K at $x = 0.05$, to 13 K at $x = 0.30$, to below 4.2 at $x = 0.35$. The superconducting transition temperature increases as x approaches the semiconducting region of $BaPb_{1-x}Bi_xO_3$. Neutron diffraction studies by Cox and Sleight[6] find a distorted perovskite structure for $BaPbO_3$ with Pb atoms occupying equivalent positions; $BaBiO_3$ has a similar structure with Bi atoms occupying two sets of octahedral sites, consistent with ordering of Bi^{3+} and Bi^{5+}. In the superconducting region the compounds have a tetragonal structure (at room temperature). Khan et al[7] do not find the tetragonal or monoclinic modifications of the perovskite structure with change in Bi concentration. Their x-ray patterns are diffuse between $x = 0$ and $x = 0.7$ which is attributed to short range order or inhomogeneities. As x increases in $BaPb_{1-x}Bi_xO_3$, the volume of the unit cell increases.

Cox and Sleight[8] have found a large anisotropy in the thermal vibrations of the oxygen ions with the amplitude perpendicular to the Bi-O bond approximately double that along the bond. They infer that these motions are consistent with the idea of a rigid oxygen octahedron surrounding the Bi ion. Moreover, Bi is found to occupy two distinct sites with average Bi-O distances consistent with the valence configuration $BaBi^{3+}_{0.5}Bi^{5+}_{0.5}O_3$. That is, in order to attain charge neutrality, which requires an average valence of 4+, Bi is equally in a 3+ and 5+ charge state. Rice and Sneddon[9] have applied a theory of the condensation of electrons, coupled to optic phonons, to $BaPb_{1-x}Bi_xO_3$ which leads to a lattice of real-space electron pairs. Anderson[10] had earlier proposed such a model whose essential feature is that strong electron-phonon coupling overcomes Coulomb-repulsion between electrons. In the Rice and Sneddon model there is an ordered superlattice, comprised of Bi^{3+} and Bi^{5+}, diluted by Pb atoms, in which electron hopping gives rise to the transport properties. Several models of the electronic structure have been proposed to account for the metal-to-semiconductor transition, and to obtain a large electron density-of-states $N(E_F)$ in the metallic phase. A large $N(E_F)$ would facilitate strong electron-phonon coupling, and, hence, a high T_c. Methfessel et al,[11] in a recent measurement of the specific heat, do not find a bulk anomaly at T_c in $BaPb_{0.75}Bi_{0.25}O_3$ and infer that the superconductivity is either not a bulk effect or a new mechanism is responsible for the superconducting behavior. However, recent ac susceptibility measurements on a single crystal of $BaPb_{0.8}Bi_{0.2}O_3$ ($T_c \approxeq 11.5$ K) suggest bulk superconductivity when contrasted with similar measurements on Nb.[12]

Batlogg et al[13] show from Meisner effect and tunneling measurements that $BaPb_{0.75}Bi_{0.25}$ is a bulk superconductor and that soft phonons can explain the negative thermal expansion and the structural transformation under pressure. L. F. Mattheiss and D. R. Harmann[14] find from electronic-structure calculations that the density of electron states at E_F is low in the concentration region where high-temperature superconductivity is found. X-ray photoemission studies by Wertheim et al[15] indicate that the occupancy of the band at E_F has predominantly oxygen 2p character.

EXPERIMENTAL RESULTS

The Mossbauer effect measurements show an isomer shift behavior (at $T \sim \theta_D$) indicating increased s-density as the metal-semiconductor boundary is approached. A decrease in the p-character of the bonding electrons, as well as an increase in s-character, would lead to this result. The composition dependence of the line width is characteristic of chemical ordering, i.e., of superlattice formation by the Bi and Pb atoms.[16] This latter result cannot be confirmed by x-ray diffraction due to the small difference between the electron-number of Pb(82) and Bi(83). Knowledge of the presence, or absence, of a Bi-Pb superlattice is important for interpreting both the composition dependence of T_c and for establishing a theoretical model of the behavior of the perovskite superconductors.

The temperature dependence of the Mossbauer effect has been made at Sn substitutions for Pb in the perovskite superconductor $BaSn_{0.03}Pb_{.67}Bi_{0.3}O_3$ (T_c = 9.4 K). This compound is the analog of that found to have a maximum T_c near the metal-semiconductor phase boundary in $BaPb_{1-x}Bi_xO_3$.[6] Figure 1 shows the Debye-Waller factor as a function of temperature. The solid line is a fit to a Debye model with θ_D = 300 K. The deviations from the Debye plot indicate lattice softening and are very similar to Mossbauer observations

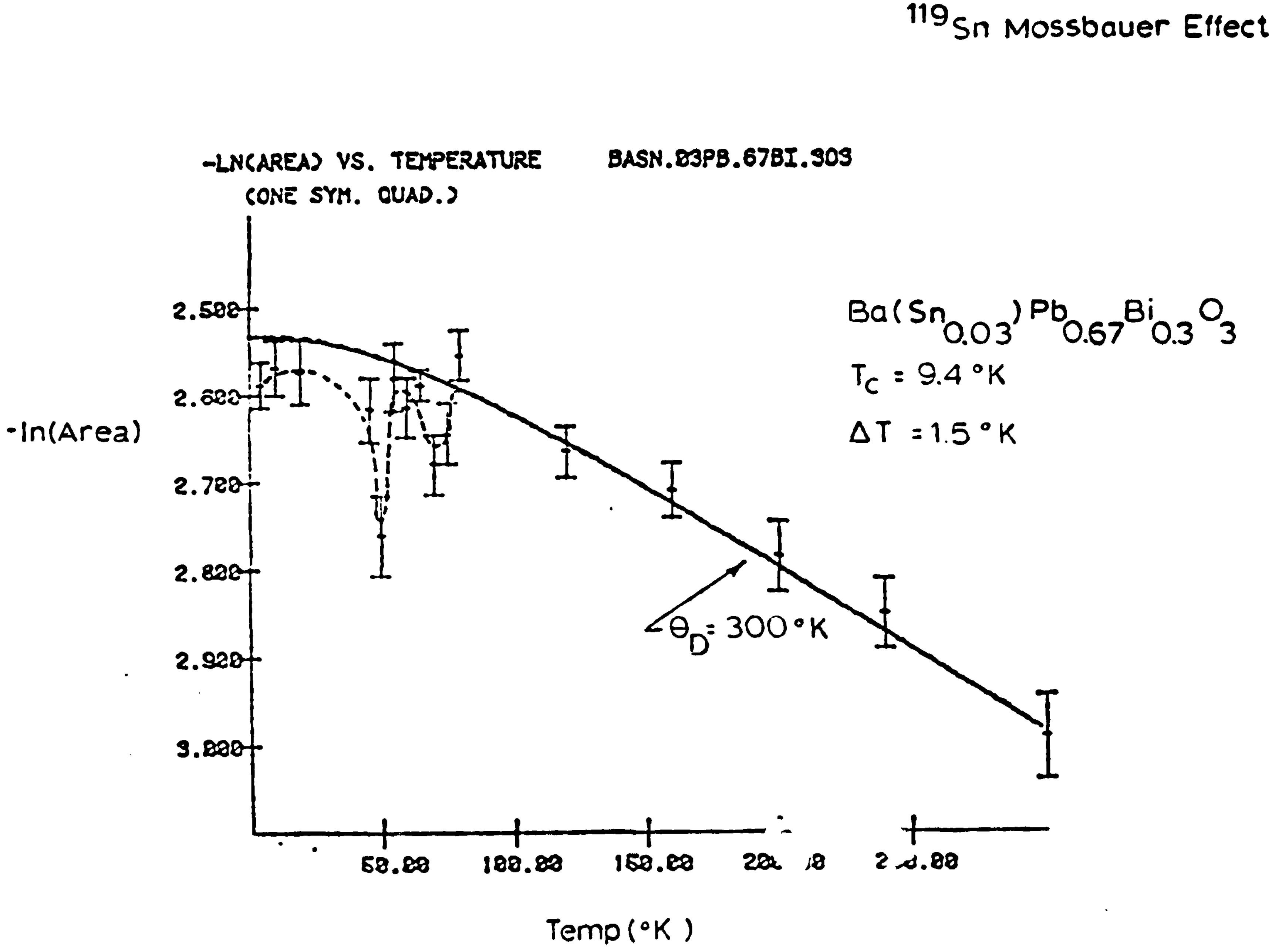


Fig. 1. Recoilfree fraction (Debye-Waller factor) vs Temperature. Solid line is fit to Debye model.

near a ferro-electric transition.[17] The thermal shift (Fig. 2) shows deviation from harmonic behavior below 75 K and indicates lattice hardening or changes in electronic structure. The low frequency modes get softer, while the high frequency modes increase their average frequency. This behavior takes place above T_c and, hence, is important for understanding the superconducting behavior.

Tin is isoelectronic and has the same valence character as Pb; Sb is isoelectronic and has the same valence character as Bi. Both Sn and Sb, however, have smaller masses then their electronic analogs and substitutions for Pb and Bi in the perovskites will affect the lattice vibrational spectrum. The ternary phase diagrams, $BaPbO_3$-$BaBiO_3$-$BaSnO_3$ (Fig. 3) and $BaPbO_3$-$BaBiO_3$-$BaSbO_3$ (Fig. 4), have been determined to establish the regions of stability of the Sn and Sb substituted compounds. The ternary is single phase only for Sn compositions less than twenty atomic percent. Small additions (0.03% Sn) have been found to extend the range of Bi concentrations over which the compounds are superconducting (Fig. 5). Although not yet confirmed, the lighter atom may also have extended the Bi concentration for which the metal-semiconductor transition takes place. As can be seen from Fig. 5, the superconducting transition temperatures remain high to x = 0.4 Bi and are comparable to the values of T_c (10% level) for our $BaPb_{1-x}Bi_xO_3$ compounds (T_c to 9.6 K).

We confirm the existence of an ordered phase, $BaSb_{0.5}Bi_{0.5}O_3$ (Fig. 6) in the Pb-Bi-Sb ternary diagram. Thornton and Jacobson[19] find a monoclinic distorted perovskite, with Sb^{5+} and Bi^{3+} valence states on the B-sites (ABO_3). The inference for the charge states is made on the basis of the Sb-O and Bi-O bond lengths which correspond to the Sb^{5+} and Bi^{3+} ionic radii. Mossbauer measurements at 4.3 K for ^{121}Sb nuclei yield definitive proof that

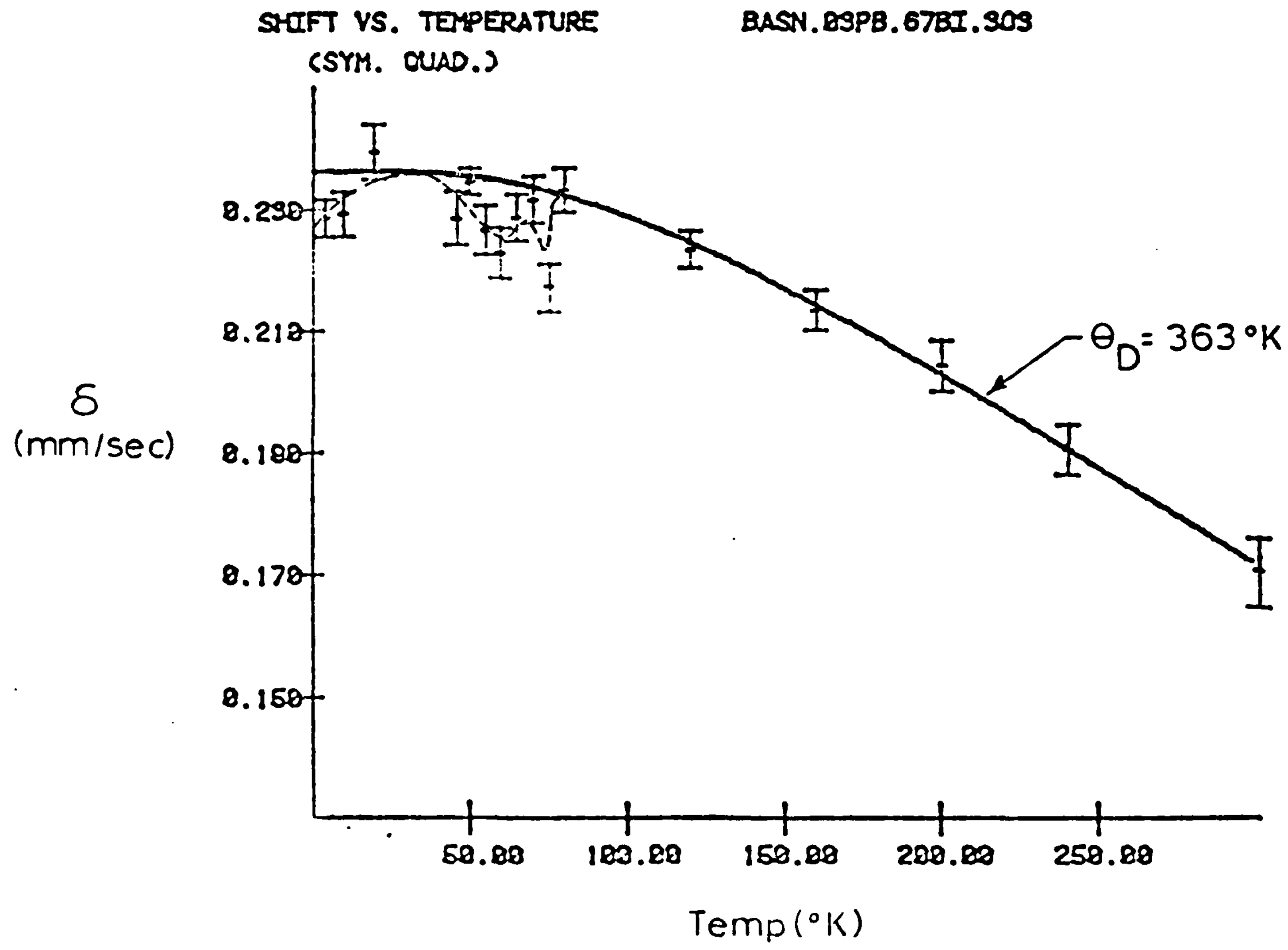


Fig. 2. Shift vs Temperature. Solid line is fit to Debye model.

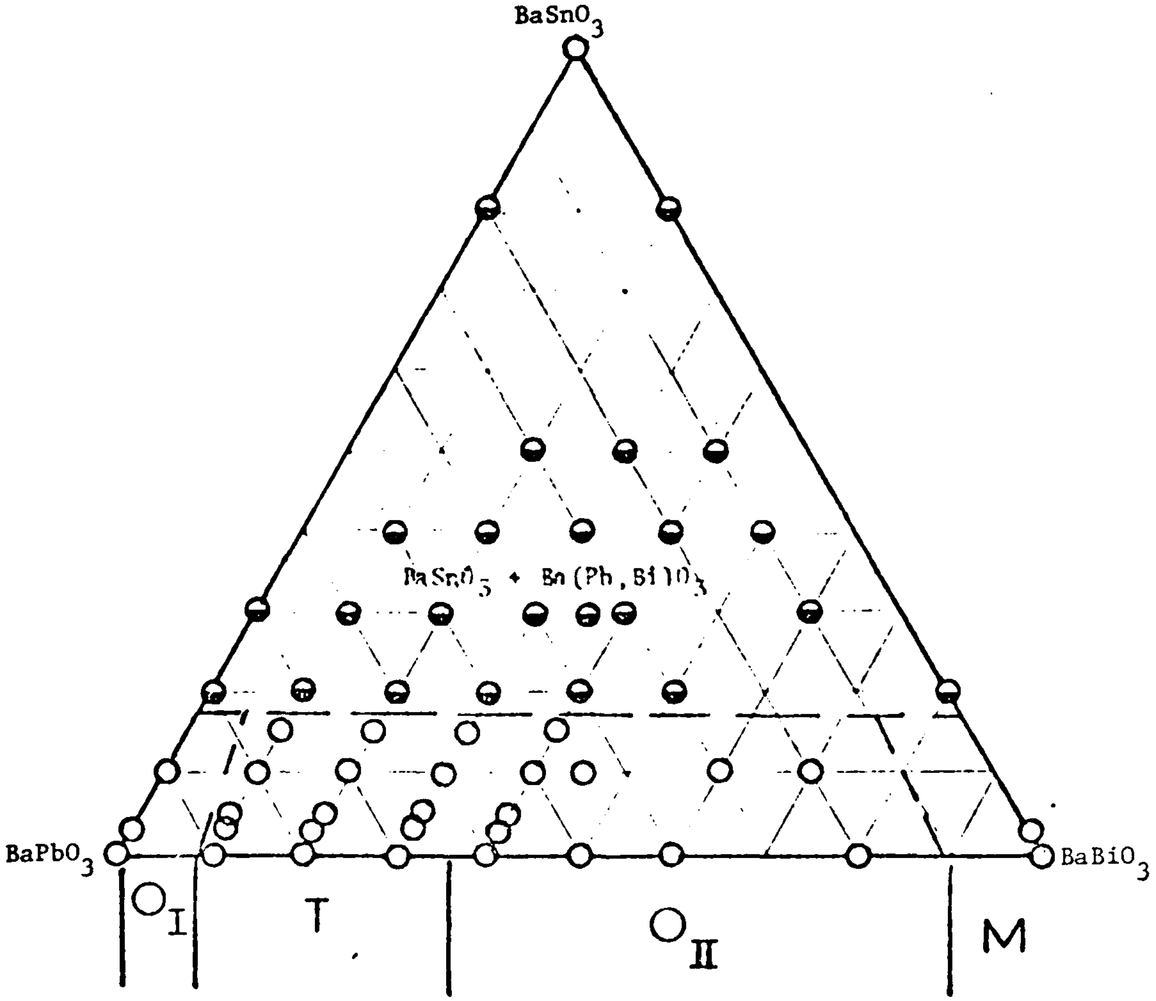


Fig. 3. Ternary phase diagram for $BaPbO_3$-$BaBiO_3$-$BaSnO_3$. Half-shaded circles indicate two-phase region.

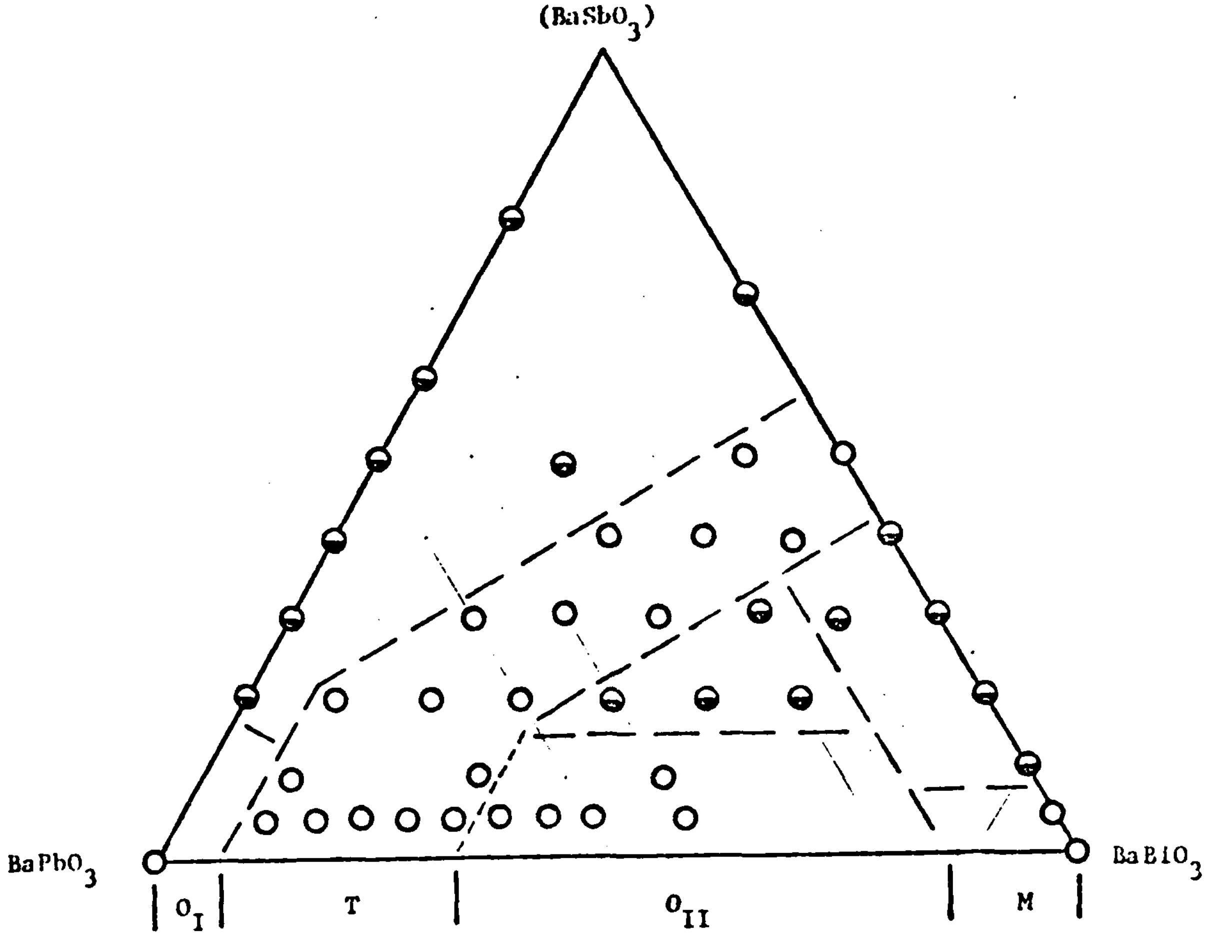


Fig. 4. Ternary phase diagram for $BaPbO_3$-$BaBiO_3$-($BaSbO_3$). $BaSbO_3$ is not stable. Half-shaded circles indicate two-phase region.

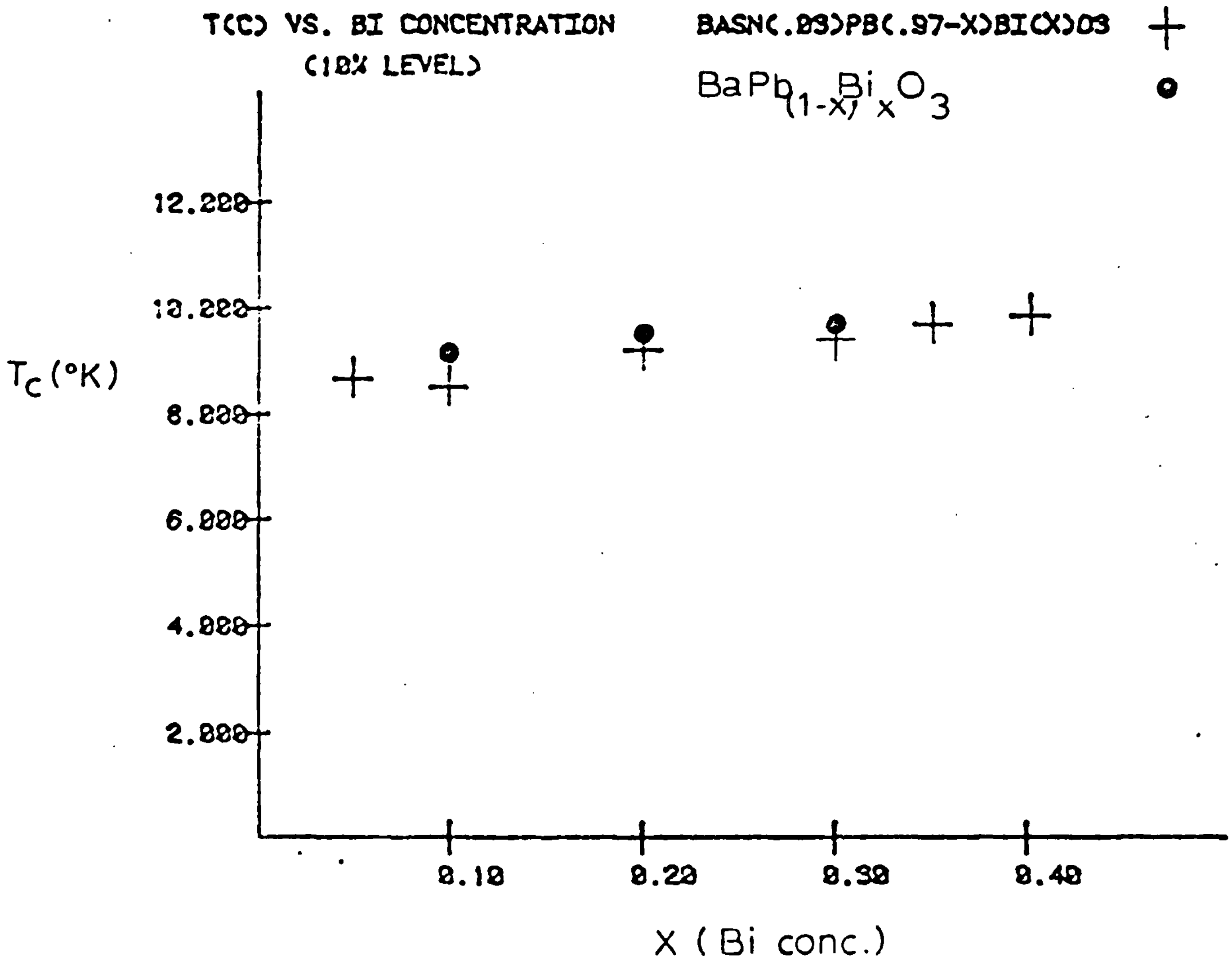


Fig. 5. Superconducting transition temperature T_c vs Bi concentration for $Ba(Sn_{0.03})Pb_{.97-x}Bi_xO_3$ compounds (+). T_c for $BaPb_{1-x}Bi_xO_3$ are indicated by solid circles (●).

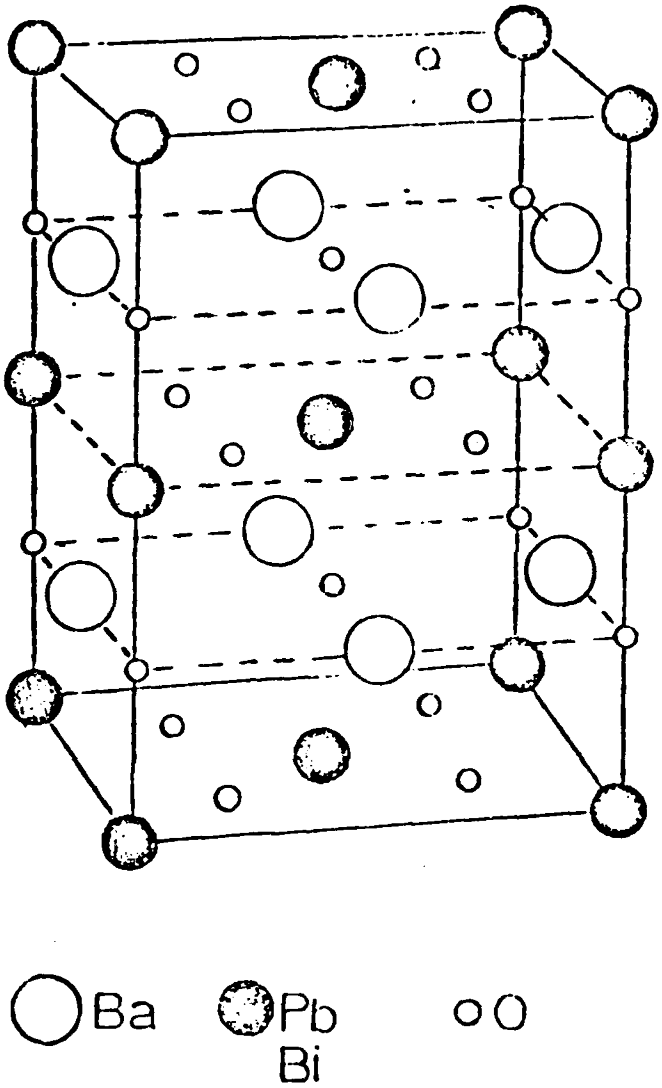


Fig. 6. Unit cell of $BaSb_{0.5}Bi_{0.5}O_3$ showing alternate ordered layers of Sb^{5+} and Bi^{3+}.

Sb takes the 5+ state; the Mossbauer spectrum for Sb_2O_3 in which Sb is 3+ and $BaSb_{0.5}Bi_{0.5}O_3$ in which Sb is 5+ are shown in Figs. 7 and 8. As can be seen from the ternary diagram (Fig. 4), there is complete solid solubility between tetragonal $BaPb_{1-x}Bi_xO_3$ and $BaSb_{0.5}Bi_{0.5}O_3$. The compounds containing 5 to 10 atomic percent antimony show tetragonal or orthorhombic distortion of the cell. At 20% Sb the Debye-Scherrer x-ray patterns show sharp lines, very little distortion and can be indexed as a cubic structure.

The substitution of 5% Sb for Bi again extends the Bi concentration for which the perovskites are superconducting (see Fig. 9). The question of whether or not the metal-semiconductor phase transition has been moved to higher Bi concentration is not yet answered. Antimony substitution for Bi does not lead to a superconducting material in $BaSb_xSb_{1-x}O_3$ for any Sb concentration. At 0.7 Pb, the concentration for the highest T_c in the $BaPb_{1-x}Bi_xO_3$ compounds, Sb substitutions to $\sim$ 0.1 retain the high T_c (as shown in Table 1).

<u>Table I.</u> Superconducting behavior for the perovskite compounds $BaPb_{1-x}Bi_xO_3$ with Sb substituted for Si.

<u>Compound</u>	<u>T_c (10% level)</u>
$BaBi_{0.95}Sb_{0.05}O_3$	None to 1.38 K
$BaBi_{0.9}Sb_{0.1}O_3$	None to 1.38 K
$BaBi_{0.5}Sb_{0.5}O_3$	None to 1.38 K
$BaPb_{0.7}Bi_{0.3}O_3$	T_c = 9.4 K ($\Delta T_c \sim$ 1.5 K)
$BaPb_{0.7}(Bi_{0.25}Sb_{0.05})O_3$	T_c = 9.6 K
$BaPb_{0.7}(Bi_{0.2}Sb_{0.1})O_3$	T_c = 9.3 K
$BaPb_{0.7}(Bi_{0.1}Sb_{0.2})O_3$	None to 4.3 K

In the Rice and Sneddon model[9] of the superconducting properties of $BaPb_{1-x}Bi_xO_3$, it is necessary for Bi to take on +3 and +5 charge states in equal numbers. One might have expected, then, that Sb would have behaved similarly. The Mossbauer spectra for ^{121}Sb at 4.3 K for high and low T_c compounds are shown in Fig. 10, Fig. 11 and Fig. 12. The Mossbauer effect measures a time-average charge fluctuation. In each case the charge state of Sb is $\sim$ 5+. On the basis of the valence fluctuation model this result requires that for each Sb substitution a Bi atom be fixed at a valence of 3+. That is, for the $BaPb_{0.7}(Bi_{0.2}Sb_{0.1})O_3$ with T_c = 9.3 K (see Table I) only half the Bi would be free to undergo valence fluctuations necessary for the hopping mechanism.

CONVERSION ELECTRON MOSSBAUER SPECTROSCOPY

Most Mossbauer effect studies of materials involve the detection of the γ-rays transmitted through absorbers. The strength of the detected Mossbauer signal is proportional to the absorption cross-section for the appropriate γ-ray:

$$\sigma_{ME} \sim \frac{\sigma_o}{1 + \alpha_T} ,$$

where α_T is the internal conversion coefficient. The number of emitted γ-rays is reduced by $1/(1 + \alpha_T)$, where α_T is greater than one. In turn approximately $\alpha_T/(1 + \alpha_T)$ electrons are emitted. For example, for ^{119}Sn, of interest here, *approximately 80% of the decays result in emission of an electron* (see Fig. 13). The K-conversion process is energetically forbidden for ^{119}Sn (E_γ = 23.88 keV, E_K = 29.2 keV) and the majority of the emitted electrons are L-conversion electrons. Hence, in principle, the signal can be enhanced by a large factor over the transmission method. Figure 13 shows the

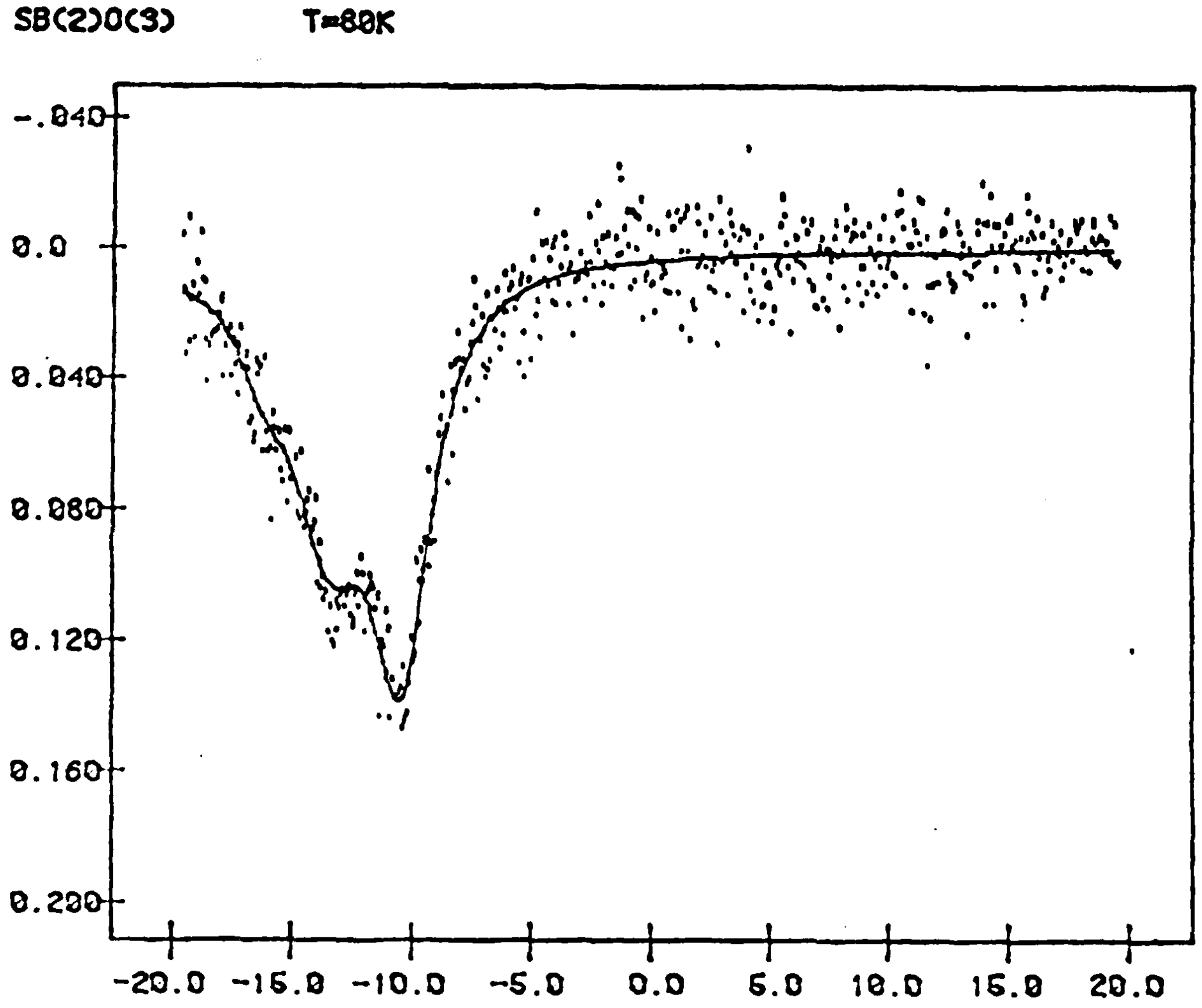


Fig. 7. Mossbauer effect at ^{121}Sb in Sb_2O_3 showing shift of Sb^{3+} valence state.

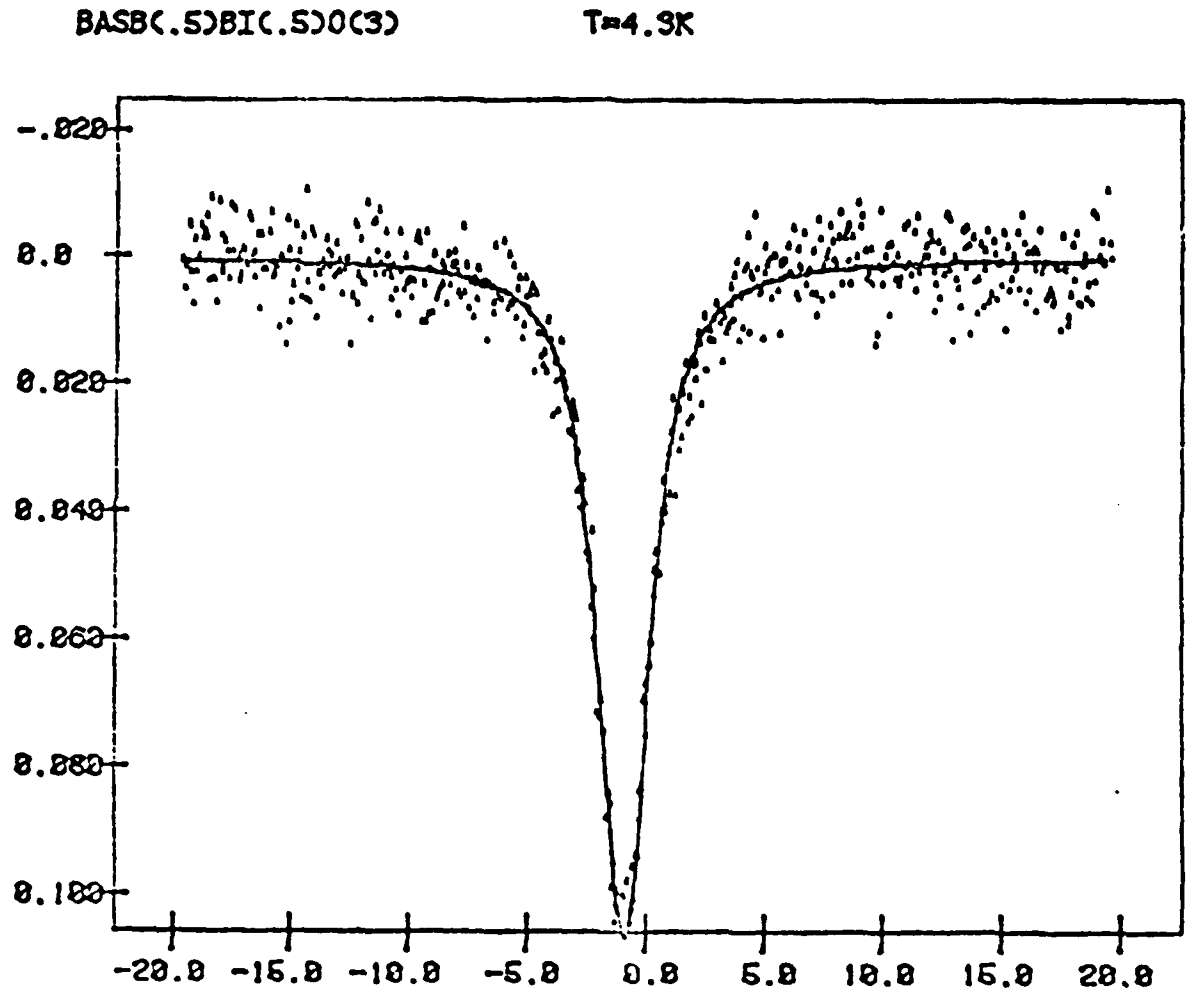


Fig. 8. Mossbauer effect at ^{121}Sb in $BaSb_{0.5}Bi_{0.5}O_3$ indicating Sb valence state of $\sim$ 5+.

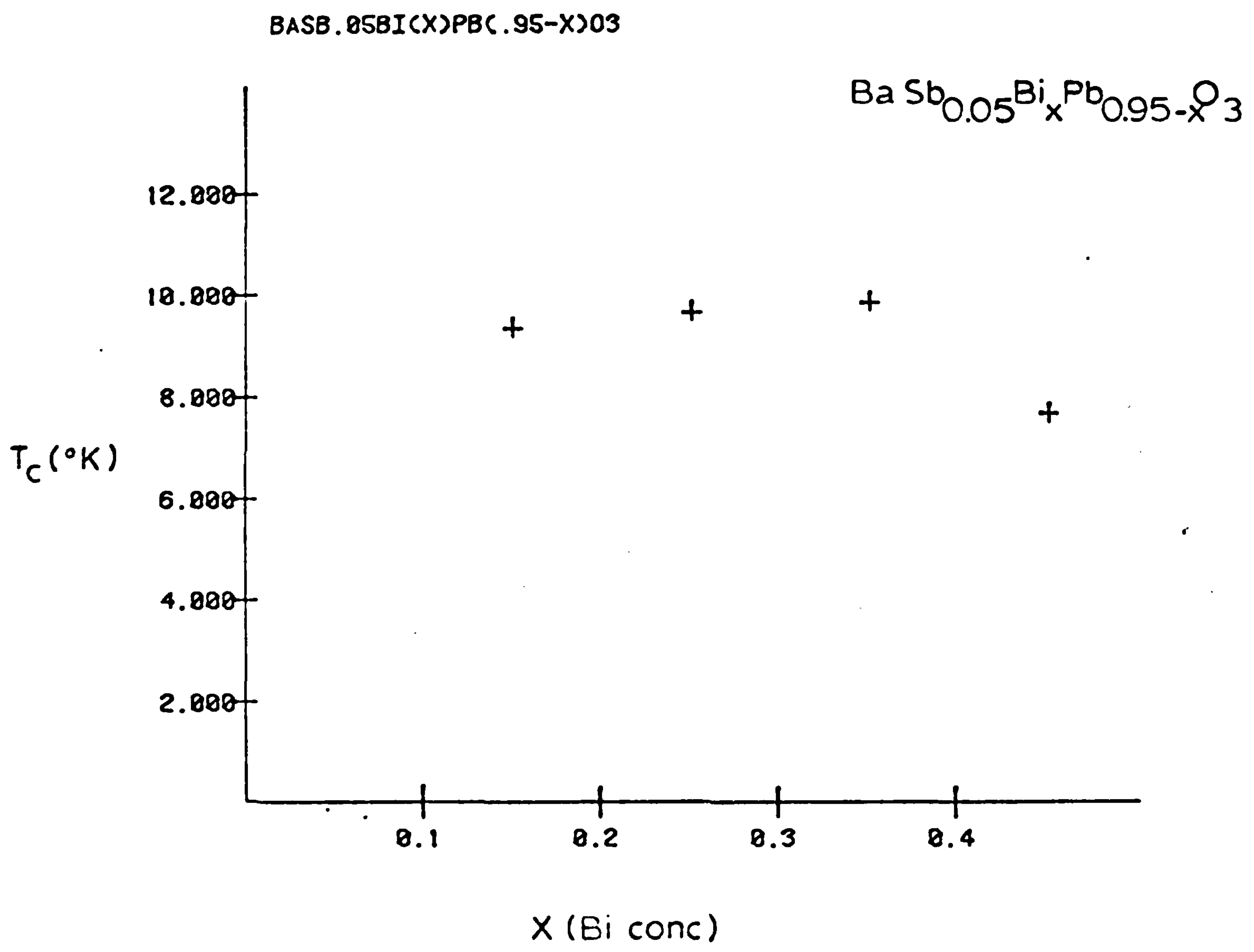


Fig. 9. Superconducting transition temperature vs Bi concentration in $BaSb_{0.05}Pb_{.95-x}Bi_xO_3$ showing extended range (> 0.3) of superconductivity.

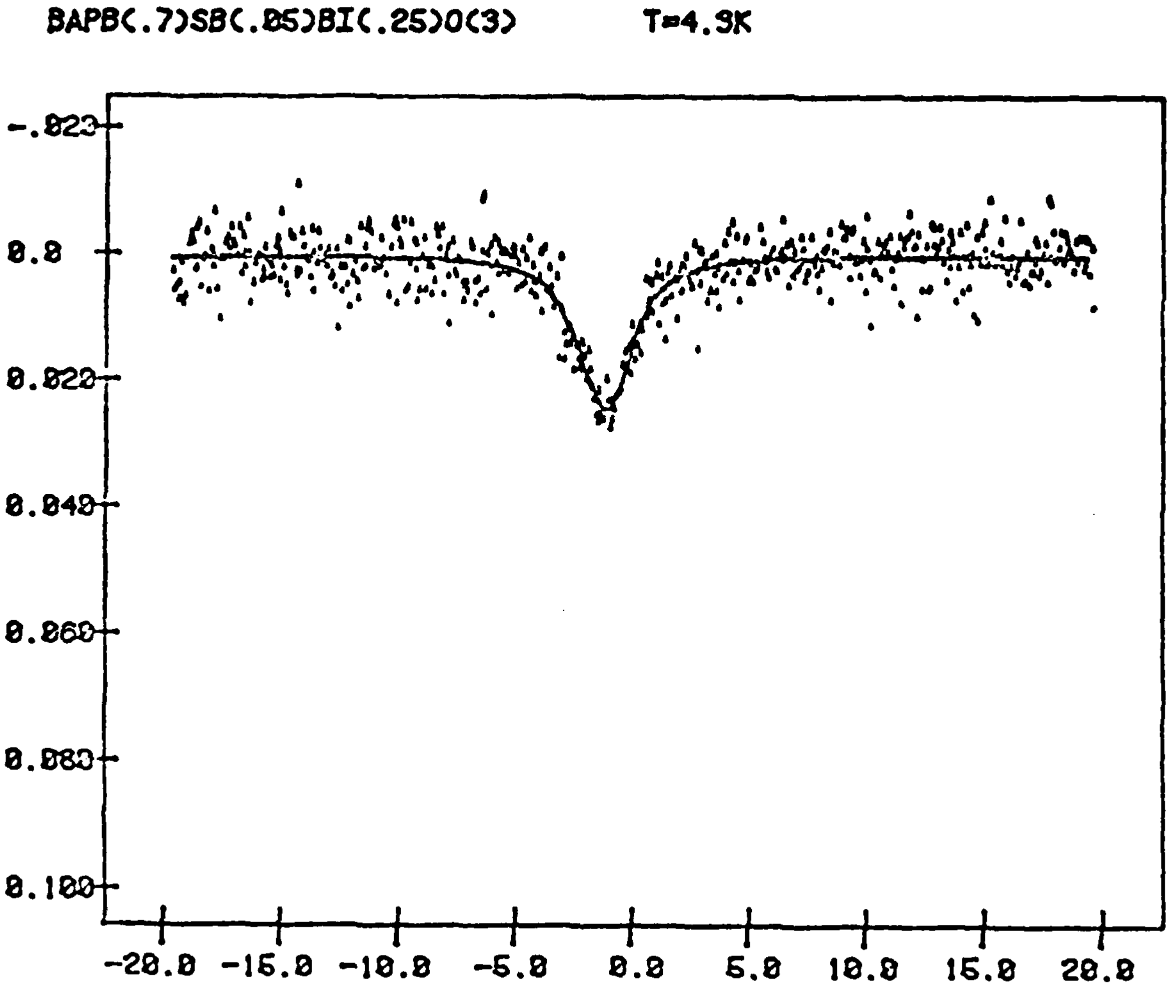


Fig. 10. Mossbauer effect at ^{121}Sb in superconducting $BaPb_{0.7}Bi_{0.25}Sb_{0.05}O_3$ indicating ∿ 5+ valence state for Sb.

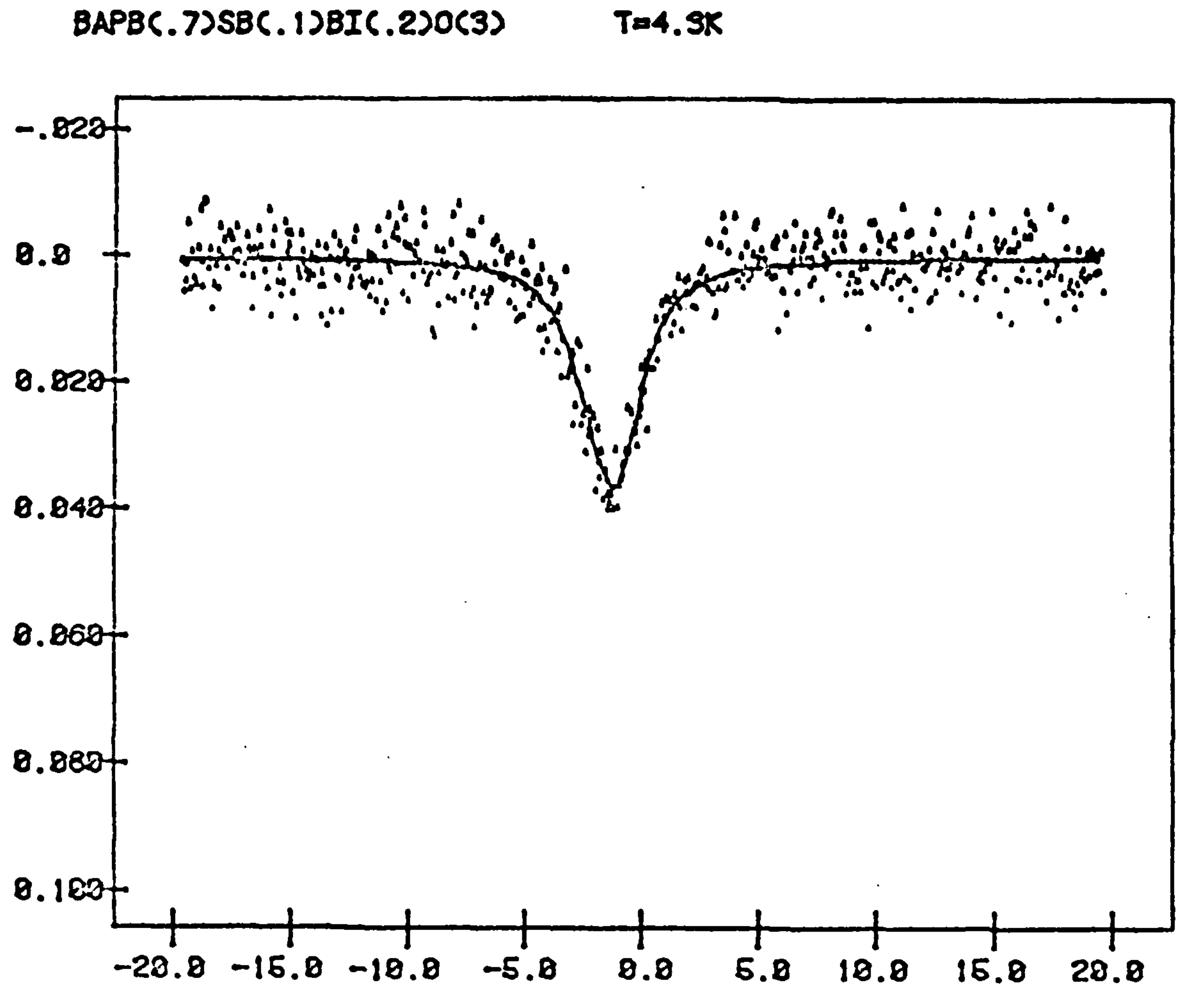


Fig. 11. Mossbauer effect at ^{121}Sb in superconducting $BaPb_{0.7}Bi_{0.2}Sb_{0.1}O_3$ indicating ∿ 5+ valence state for Sb.

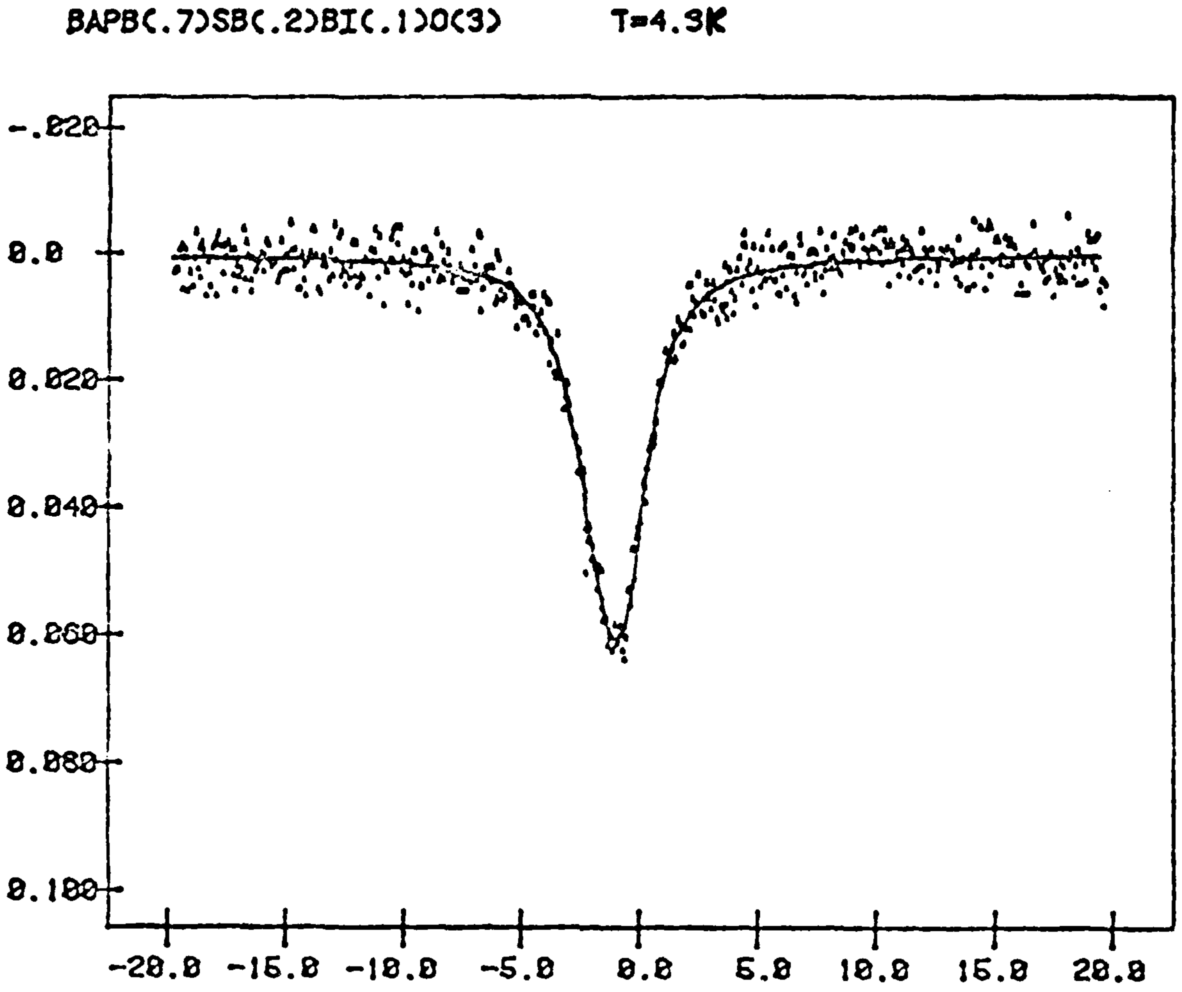
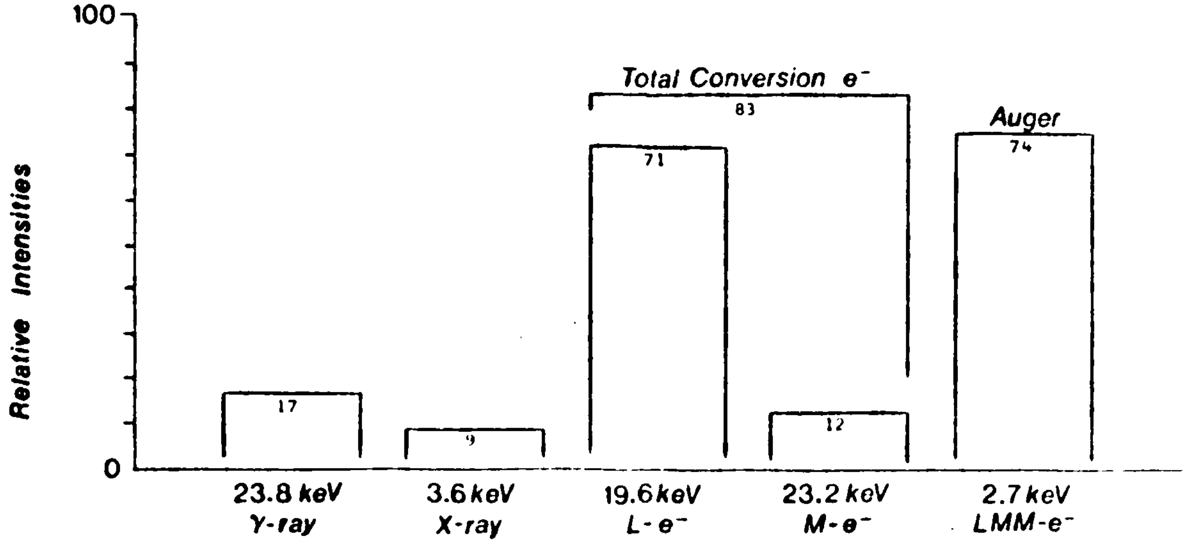


Fig. 12. Mossbauer effect at ^{121}Sb in non-superconducting $BaPb_{0.7}Bi_{0.1}Sb_{0.2}O_3$ indicating ∿ 5+ valence state for Sb.



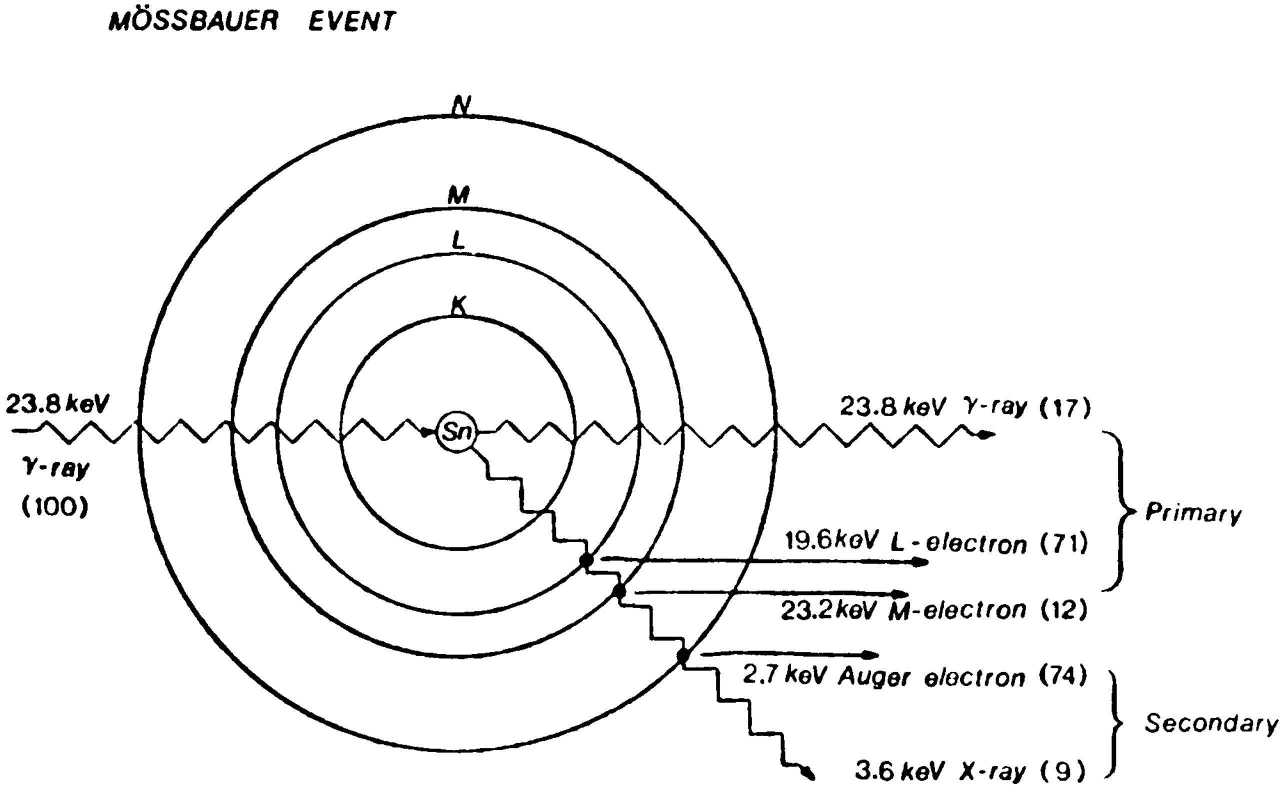


Fig. 13. Radiation from ^{119}Sn Mossbauer isotope.

relative intensities of the various processes and diagrammatically indicates the mechanism of emission.

The converted electrons have a much smaller range in the material than the x-rays; for example, an approximate maximum range for the L-electron from ^{119}Sn is 2.4 μm. Hence, the depth of the probe in a material depends on the energy spectrum of the electrons produced during the Mossbauer decay and on the energy selected for detection. (For ^{57}Fe, the K-conversion energy is 7.3 keV and the approximate maximum range is 0.25 μm; the M-conversion 13.6 keV and range 0.9 μm.) The majority of studies done with this technique have been designed to examine 'surfaces'.[18] It is clear, however, that depths of 2.4 μm (24000 Å) or 0.25 μm (2500 Å) in a material constitute bulk not the surface.

Conversion Electron Mossbauer Spectroscopy (CEMS) is conventionally done with the sample mounted inside a gas-flow counter which greatly restricts the temperature range over which measurements can be made.[19] We have constructed a simple gas flow proportional counter and have made room temperature CEMS measurements for Nb_3Sn films. Even though the sample size is 40 times smaller than those for transmission measurements, the signal strength is three to four times greater with no thickness broadening (see Fig. 14). A study was initiated in collaboration with T. Geballe of Stanford University to examine the effects of varying stoichiometry and of inserting interstitial oxygen on the lattice behavior of Nb_3Sn superconducting films.

Without the possibility of making measurements over a wide temperature range, the vibrational properties of interest could not be discerned. An electron detector was obtained which operates in vacuum and which allows the absorber temperature to be varied from ∿ 2 K to above room temperature. A conversion electron Mossbauer spectrometer with temperature variability was

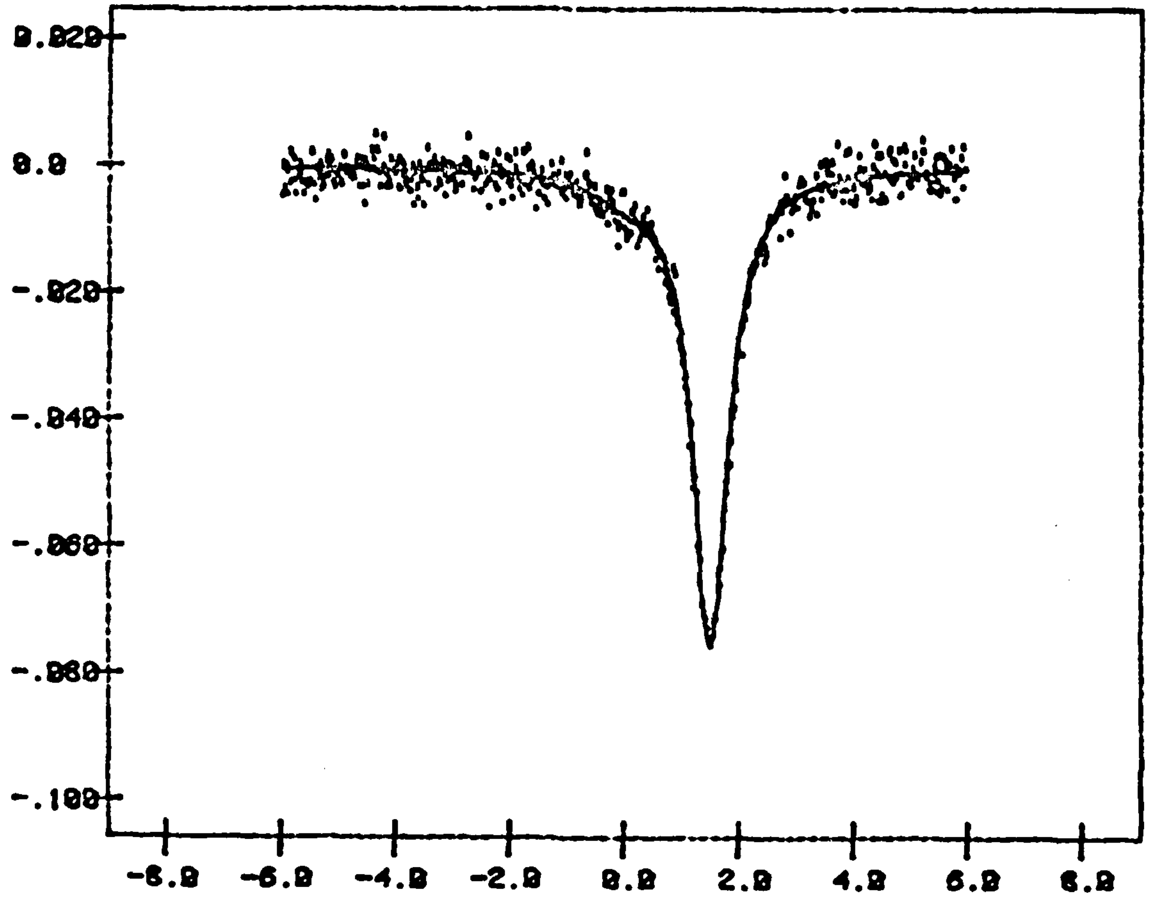


Fig. 14. Conversion Electron Mossbauer spectrum of Nb_3Sn at 300 K. The effect is ∿ 8% from a 2.5 μm film whose dimensions are about 4 mm x 4 mm. A small quantity of surface oxide is observed near zero velocity.

designed and developmental studies made to optimize the experimental parameters. The ability to make temperature dependent measurements will enable one to monitor phase stability and phonon softening in films which have important electronic applications.

What is clear is that the CEMS technique provides a unique probe of the lattice vibrational and structural properties of thin films (and magnetic properties as well!). Moreover, small quantities of surface oxides, minute quantities of second, or new phases created by the microchemistry of thin film formation can be detected.

SUMMARY

The temperature dependence of the Mossbauer absorption was measured at ^{119}Sn nuclei in the perovskite superconductor $Ba(^{119}Sn_{0.03})Pb_{0.67}Bi_{0.3}O_3$. $BaPb_{0.7}Bi_{0.3}O_3$ is superconducting with a T_c onset of 13 K. Three atomic percent of tin, isoelectronic but of smaller mass, was substituted for Pb; T_c for the Sn substituted compound is 9.4 K (10% level). The mean-square displacement ($\sim \langle\omega^{-1}\rangle$) derived from the Mossbauer recoilfree fraction deviates from Debye behavior near 75 K, near 50 K and below 20 K, and is characteristic of phonon softening in ferroelectrics. However, x-ray diffraction patterns, which have broad Bragg lines at room temperature, are essentially unchanged at 5 K. The Mossbauer shift ($\sim \langle\omega\rangle$) also deviates from Debye behavior near 60 K and below 20 K in a direction consistent with either a decrease in the s-density on the Sn atom or a simultaneous hardening of the high frequency modes.

Mossbauer measurements were made at ^{119}Sn nuclei in $Ba(^{119}Sn_{0.03})Pb_{.97-x}Bi_xO_3$ for x = 0, 0.05, 0.1, 0.2, 0.3, 0.35, 0.4 and 0.97. The bismuth-rich perovskite is a semiconductor, the lead-rich compound metallic. The $BaPb_{1-x}Bi_xO_3$ system is superconducting for Bi concentrations between x = 0.05 and 0.3. The addition of 0.03 Sn extended the range of Bi concentration for which these compounds retain superconducting properties; the superconducting transition temperature (10% onset) increases from 8.5 K for x = 0.05 to 9.8 K for x = 0.4. The superconducting behavior is complex for higher Sn concentrations. The shifts vs composition for the superconducting compounds indicate that the s-electron density at the Sn nucleus increases as T_c increases. The effect of Sb substitution for Bi on the superconducting properties of the perovskite compounds $BaPb_{1-x}Bi_xO_3$ was investigated. Small quantities of Sb extend the composition range of superconductivity. For 0.05 Sb the transition temperature (10% onset) rises from 9.3 K at 0.15 Bi, to 9.8 K at 0.35 Bi; T_c drops to 7.6 K at 0.45 Bi. For 0.7 Pb, T_c is 9.6 K at 0.05 Sb, 9.3 K at 0.1 Sb and below 4.3 K at 0.2 Sb. Mossbauer measurements at ^{121}Sb nuclei were made for both superconducting and non-superconducting compounds. The valence state of Sb is $\sim 5^+$ for all concentrations.

Preliminary work for a program to examine the origin of the 'remarkable enhancement' of superconducting properties in eutectic systems motivated studies of the preparation and characterization of these eutectic materials. The net result was that the reported enhanced properties were properly attributed to previously unknown second phases and were not a property of the formation of a eutectic material.

In pilot studies of the application of Conversion Electron Mossbauer Spectroscopy to thin film superconductors, it was found that this technique provides a unique tool for determining the lattice vibrational properties, including phase stability and phonon softening, of thin film materials.

REFERENCES

1. T. A. Kitchens, P. P. Craig and R. D. Taylor, in Mossbauer Effect Methodology V5, ed. I. J. Gruverman, p. 123; C. W. Kimball, S. P. Taneja, L. Weber and F. Y. Fradin, ibid V9, p. 93.

2. C. W. Kimball, L. W. Weber and F. Y. Fradin, Phys. Rev. B14, 2769 (1976).

3. D. C. Johnston, H. Prakash, W. H. Zachariasen and R. Viswanathan, Mat. Res. Bull. 8, 777 (1978).

4. B. T. Matthias, Ternary Superconductors, ed. G. K. Shenoy, B. D. Dunlap and F. Y. Fradin (North-Holland Publishing Co., Amsterdam, 1981).

5. A. W. Sleight, J. L. Gillson and P. E. Bierstadt, Solid State Comm. 17, 27 (1975).

6. D. E. Cox and A. W. Sleight, Proceedings of the Conference on Neutron Scattering VI, Gatlinburg, Tenn., June 1976, p. 45.

7. Y. Khan, K. Nahm, M. Rosenberg and H. Wilner, Phys. Stat. Sol. 39, 79 (1977).

8. D. E. Cox and A. W. Sleight, Acta Cryst. B35, 1 (1979).

9. T. M. Rice and L. Sneddon, Phys. Rev. Lett. 47, 689 (1981).

10. P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

11. C. E. Methfessel, G. R. Stewart, B. T. Matthias and C. K. N. Patel, Proc. Nat. Acad. Sci., U.S.A., 77, 6307 (1980).

12. J. P. Remeika, B. Batlogg, F. DiSalvo, A. S. Cooper and H. Barg, Bull. Am. Phys. Soc. 27, 318 (1982).

13. B. Batlogg, J. P. Remeika, R. C. Dynes, A. S. Cooper and J. P. Garno. Conference of Low Temperature Physics, Karlsruhe, Germany, 1982.

14. L. F. Matthiess and D. R. Harmann (to be published).

15. G. K. Wertheim, J. P. Remeika and D. N. E. Buchanan, Phys. Rev. B26 (1982).

16. C. W. Kimball, T. F. Karlov, B. L. Stafford, A. T. Aldred and F. Y. Fradin, Bull. Am. Phys. Soc. 26, 342 (1981).

17. C. N. R. Rao and K. J. Rao in Phase Transitions in Solids (McGraw-Hill, New York, 1978), p. 291 (and references on p. 320).

18. M. Lyon and G. Zepp, Can. J. Phys. 55, 55 (1977); and references therein.

19. M. J. Tricker, Mossbauer Spectroscopy and its Chemical Applications, ed. John G. Stevens and Gopal K. Shenoy (American Chemical Society, Washington, D. C., 1981), p. 63.

PUBLICATIONS

"High Temperature Mossbauer Study of ^{57}Fe Interstitials in Chevrel Phases," Ternary Superconductors (North-Holland-Elsevier Publishing Co., NY, 1981) ed. G. K. Shenoy, B. D. Dunlap and F. Y. Fradin. With B. L. Stafford, T. F. Karlov and F. Y. Fradin.

"Mossbauer Study of the Electronic and Vibrational Properties of Sn- and Sb-Substitutions in the Perovskite Superconductor $BaPb_{1-x}Bi_xO_3$," Superconductivity in d- and f-band Metals, ed. W. Buckel and W. Weber, Kernforschungszentrum Karlsruhe GmbH, Karlsruhe, Germany, 1982). p. 409. With A. E. Dwight, S. K. Farrah, T. F. Karlov, D. J. McDowell and S. P. Taneja.

"Mossbauer Study of the Phase Stability of Oxide Superconductors" (to be submitted to The Physical Review).

"Valence Behavior of ^{121}Sb in High T_c Oxide Superconductors" (to be submitted to The Physical Review).

Professional Talks

"High Temperature Mossbauer Studies of ^{57}Interstitials in Chevrel Phases," Conference on Ternary Superconductors, Lake Geneva, Wisconsin, September 1980.

"Phonon Softening above T_c in Superconducting $BaPb_{0.67}Bi_{0.3}O_3$," American Physical Society, Dallas, Texas, March 1982.

"Superconducting Behavior of $BaPb_{1-x}(Bi,Sb)_xO_3$ Compounds," American Physical Society, Dallas, Texas, March 1982.

"Mossbauer Study of the Superconducting Perovskites $Ba(Sn,Pb)_{1-x}Bi_xO_3$," American Physical Society, Dallas, Texas, March 1982.

"Mossbauer Study of the Electronic and Vibrational Properties of Sn- and Sb-Substitutions in the Perovskite Superconductor $BaPb_{1-x}Bi_xO_3$," Fourth Conference on d- and f-band Superconductivity, Karlsruhe, West Germany, July 1982.

"Mossbauer and X-ray Studies of the $BaPbO_3$-$BaSnO_3$ and the $BaPbO_3$-$BaBiO_3$-($BaSb_2O_6$) Systems," Materials Research Society, Boston, Massachusetts, November 1-4, 1982.

"Mossbauer Study of Structural Stability of Oxide Superconductors," Materials Research Conference, Argonne National Laboratory, October 1983.

bjs

END

FILMED

8-84

DTIC