207Pb AND 17O NMR STUDY OF THE ELECTRON DENSITY DISTRIBUTION IN METAL PHASE OF BaPb1−xBi2O3

Yu. Piskunov, A. Gerashenko, A. Pogudin, A. Ananyev, K. Mikhailov, K. Okulova and S. Verkhovskii
Institute of Metal Physics, UB RAS, Ekaterinburg, Russia

A. Yakubovsky
Russian Research Centre "Kurchatov Institute", Moscow, Russia

A. Trokiner
Laboratoire de Physique du Solide, E.S.P.C.I., Paris, France

The 17O and 207Pb NMR spectra were measured in ceramic samples in the metallic phase of BaPb1−xBi2O3 oxides (0 < x ≤ 0.33). The inhomogeneous magnetic broadening which appears due to a distribution of the Knight shifts was analyzed in detail. It is shown that Bi atoms, which are randomly incorporated in BaPbO3 parent compound give rise to an increased conduction electron spin density within an area which is delimited by its two first cation shells. According to NMR data the percolative overlap of these areas occurs in superconducting compositions and it is accompanied by a sharp growth of the average Knight shift with temperature revealed for x = 0.33 evidences for an opening of the energy gap near EF near the metal-semiconductor transition (x = 0.35).

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I. INTRODUCTION

During the last two decades many studies have been devoted to the electron states in the conduction band of superconducting BaPb1−xBi2O3 oxides (BPBO). Substituting Bi for Pb in the metallic parent compound, BaPbO3, leads to pseudo gap compounds in the composition range 0.1 < x < 0.33 (superconducting composition range, SCR). The density of states at Fermi level N(EF) is found to be small and Ts, the superconducting transition temperature, estimated from thermal capacity data in the Debye approximation is substantially smaller than observed ≥0.8. According to extended photo-emission studies a pseudo gap near EF appears for x ≥ 0.2 and exists as a real gap for semiconducting compositions (x > 0.35). Finally, the end member of the family, BaBiO3, is an insulator with an energy gap ∼1eV due to the commensurate charge density wave (CDW) breathing mode (qa = {π, π, π}) developed in the Bi6-octahedra sublattice. It was considered that electron-phonon coupling might be increased due to the breathing phonon mode existing in SCR as the short-wave change fluctuations. Exclusively electronic origin of the attractive retarded coupling between the carriers due to the "skipped valence" effects of Bi was proposed by Varma and the relevant phase diagram was developed in for semiconducting phase of bismuthates. However the stability of a uniform electron system in a metallic phase in the presence of random ion potential due to the cation disorder is still an open question. As noted in Ref. the changes in the carriers motion near the more electronegative Bi cations can lead to an electronic ground state associated to a non uniformly distributed electron system in the real space.

Most of the experimental data concern parameters describing the electronic and structural properties of an averaged crystal. The static and dynamic effects of the cation disorder in the sublattice of Pb(Bi)O6 octahedra on conduction electrons are considered only in few publications. In discussing neutron diffraction results it was concluded that in the range of 0.12 < x < 0.3, the crystal structure of BaPb1−xBi2O3 can be considered as a micro-dispersed mixture of tetragonal and orthorhombic phases. Furthermore, a reversible change of the relative fraction of the two phases occurs with temperature. EXAFS13 and 173Ba NMR&NQR14 studies have confirmed the presence of local lattice distortions in the Bi(Pb)O6 sublattice. The influence of short-range ordering of Bi cations in regard to the developed electron instability was studied in Ref. It was shown that some specific configurations of cations give rise to non-metallic cluster for metallic compositions x > 0.1.

Being a local probe of electronic properties, Nuclear Magnetic Resonance (NMR) is well suited to determining the spatial distribution of electric and magnetic fields of non homogeneous structures. The Knight shift 207Ks and spin-lattice relaxation rate 207T−1 of lead were measured at T = 4K in BaPbO3. The behavior of these properties is similar to the one of normal metals and 207Pb NMR studies show a monotonous increase of the Knight shift Ks ∼ N(EF) as a function of x when approaching the metal-semiconductor transition and no evidence for electron correlation effects was reported for composition x = 0.22 which corresponds to the highest Tc, Tc,max = 12.5K. It is worth to note that aforementioned NMR data were analyzed assuming that all the oxygen and lead ions are located in magnetically equivalent sites of the ideal crystal, ignoring any disorder. Only
an abnormally broad distribution of the $^{207}$Pb NMR line shift in SCR for $0.10 < x < 0.18$ was attributed to the effect of CDW instability developed in the oxides placed compositionally close to the metal-semiconductor transition boundary ($x = 0.35$).

Taking into account these results we carried out a detailed study of $^{17}$O and $^{207}$Pb NMR for BaPb$_{1-x}$Bi$_x$O$_3$ in the metallic region ($0 \leq x \leq 0.1$) as well as in the superconducting region ($0.1 \leq x \leq 0.36$). The analysis of NMR spectra evidences the formation and evolution of a microscopic inhomogeneous distribution of the charge and spin densities of mobile carriers in these compositions.

II. EXPERIMENTAL

The measurements were performed on single-phase powder samples BaPb$_{1-x}$Bi$_3$O$_3$ (BPBO) in the range, $0 \leq x \leq 0.36$. The BPBO samples were prepared with the following compositions, $x = 0.36, 0.33, 0.27, 0.21, 0.18, 0.15, 0.12, 0.09, 0.03$ and $0$. The samples were obtained by the conventional solid-state reaction in air similar to that described in Ref. The powder was poured into a platinum cup and placed into a quartz tube with flowing $^{17}$O$_2$ mounted in the furnace. During the heat treatment the oxygen gas in the quartz loop was continuously scrubbed with Ascarite and cold plate (at 180°C) for 168 hours under an oxygen pressure of 730 Torr. The system was filled twice with $^{17}$O isotope. The sample was then cooled to $T = 300K$ with a rate of 15K/hour. According to mass spectroscopic analysis, the final $^{17}$O enrichment of the sample was about 15%. During the preparation and the enrichment the cooling rate used was always slow enough to obtain samples with the minimal amount of oxygen vacancies.

The x-ray powder diffraction measurements were performed at $T = 300K$ with a DRON4-A diffractometer with CuK$_\alpha$ radiation in the range of $2\theta = (10-70)$ degrees. To minimize the instrumental error in determining the positions of Bragg reflexes the sample was mixed with a powder of crystalline germanium. The best fit of experimental x-ray diffraction patterns was found when assuming orthorhombic symmetry of the unit cell parameters for all compositions. No other peaks evidencing the presence of spurious phases in the samples were revealed. A monotonous decrease of the unit cell volume is deduced as x increases. The structural parameters of the samples are in a good agreement with the data published in Ref.

$T_c$ was determined with ac and dc magnetic susceptibility measurements (Fig 1). The superconducting transition width does not exceed $2K$ for $x = 0.25$. The superconducting volume fraction was estimated from the magnetization $M(T)$. It was measured by field cooling (FC) and zero field cooling (ZFC) experiments with a SQUID-DESIGN device operating at $B_0 = 10^{-3}T$ (inset in Fig.1). The deduced Meissner fraction exceeds 0.8 for $x = 0.15$ and $x = 0.27$. For $x > 0.3$ and $x < 0.15$ the superconducting response is absent down to $4K$. Concerning the homogeneity of composition, the x-ray analysis and dc-magnetization data are in favor of a high enough homogeneity on macroscopic scale for all the samples.

$^{207}$Pb and $^{17}$O NMR measurements were carried out on a Bruker NMR pulse spectrometers over the temperature range of $10 - 350K$ in 3 magnetic fields, 2.0, 9.1 and 11.7T. The spectra were obtained by Fourier transformation of the second half of the echo signal obtained with the $(\pi/2)_x - \tau_{del} - (\pi)_x$ pulse sequence. A phase cycling of the pulses was used in order to suppress spurious signals arising from the transient rings in the rf-circuit after the pulses. The spectra for which the width exceeds the frequency band excited by the rf-pulse were obtained by irradiating the whole spectrum at equidistant frequencies. The spectrum was reconstructed after Fourier transformation of the corresponding echoes.

The components of the magnetic shift tensor ($K_{iso}$, $K_{ax}$) for $^{17}$O and $^{207}$Pb as well as the electric field gradi-
ent (EFG) parameters (for $^{17}\text{O}$) - quadrupole frequency, $\nu_Q$, and asymmetry parameter, $\eta$, - were determined by computer simulation of the measured NMR spectra. The powder pattern simulation program takes into account the quadrupole coupling corrections up to the second order of the perturbation theory. The NMR powder pattern is calculated with a distribution function of the NMR parameters and a non-uniform broadening of the spectra can be specified.

For $^{17}\text{O}$, the positions of the features of both, the central line (transition $m = -\frac{1}{2} \leftrightarrow +\frac{1}{2}$) and satellite lines ($m = \pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$), were analyzed. We used solid Pb$^{11+}$$(\text{NO}_3)_2$ for $^{207}\text{Pb}$ ($^{207}\nu_L = 80.978\text{MHz}$) and H$_2\text{O}$ for $^{17}\text{O}$ as frequency references.

Above $T_c$ the magnetic susceptibility $\chi_m$ was measured by a Faraday balance technique. The measurements were performed in the temperature range of $4.2 - 370K$ in a magnetic field of $0.5T$ and the instrumental error did not exceed $0.02 \chi_m$.

![FIG. 2: $^{207}\text{Pb}$ NMR spectra of BaPb$_x$Bi$_{1-x}$O$_3$ measured by spin echo technique with different delay time $\tau_{del}$ between echo pulses.](image)

![FIG. 3: Relative intensity of the narrow peak $^{207}\text{Int}_B$ and width line C $\Delta K_c$ as a function of $x$ in $^{207}\text{Pb}$ NMR spectra of BaPb$_{1-x}$Bi$_x$O$_3$.](image)
III. EXPERIMENTAL RESULTS AND DISCUSSION

A. $^{207}$Pb NMR spectra

The $^{207}$Pb NMR spectra shown in Fig.2 for BPBO samples were obtained at $B_0 = 9.17$, in the temperature range of $5 - 20K$. For SCR, spectra were measured in the normal state since $B_0$ exceeds the critical field, $H_c$. A single non uniformly broadened line (Line A) is found at low frequency in the semiconducting region, $x > 0.35$, (Fig.2a). Its shift $^{207}K(0.36)$=0.30 (5)% is in the range of chemical shifts reported for Pb$^{+IV}$ in insulating oxides $\text{Ba}_2\text{PbO}_4$ (0.21%) and $\text{Sr}_2\text{PbO}_4$ (0.23%). Line A still exists in SCR but its intensity sharply decreases with decreasing $x$. For $x = 0.12$ the relative intensity of line A is less than 5% of the total intensity of $^{207}$Pb spectrum. Even for $x = 0.36$, less than one third of the lead atoms contribute to the line A (Fig.2a). Its shift is independent on both, $T$ and $x$. Its spin-lattice relaxation time $T_1$ is of order of 1$s$ and the spin-spin relaxation time $T_2$ is about $75(10)$µs at $T = 20K$. At the moment we cannot definitely judge on the origin of this line in SCR. The measurements on semiconducting compositions of BPBO (0.4 ≤ $x$ ≤ 0.9) are planned to clear up this point.

On the end of the phase diagram, in $\text{BaPbO}_3$, a single, nearly gaussian, symmetric line (line B) is detected at higher frequency (Fig.2). Its shift, 0.91(2)% is $T$-independent and is in quite a good agreement with published data in $\text{BaPbO}_3$. As shown in Fig.2b, the high frequency part of the NMR spectra in the Bi-containing compounds depends strongly on the delay time $\tau_{del}$ between rf-pulses. In order to analyze the spectra obtained in metallic compounds ($x < 0.35$), let us focus on the main features of the $^{207}T_2$ behavior in the high frequency part of the spectra.

(i) In $\text{BaPbO}_3$ the value of $^{207}T_2^{-1}$ exceeds greatly the homonuclear magnetic dipole contribution $^{207}T_2^{-1}_{\text{dip}} \approx (0.1 - 0.3)\text{ms}^{-1}$ estimated for sample with natural abundance of the lead isotopes. In $\text{BaPbO}_3$ and $x = 0.09$ samples, $^{207}T_2(5K) = 55(5)\mu$s. Besides, the intensity of the echo, $I(2\tau_{del})$, demonstrates an oscillating behavior at low temperature with $\omega_{osc} = 4.5(5) \cdot 10^5$s$^{-1}$. The homonuclear indirect coupling term $J_{\text{ex}}\text{I}_{1-1}\text{I}_{1-2}$ is assumed to be responsible for the $^{207}T_2$ in the metallic phase. The exchange integral for $\text{BaPbO}_3$ estimated within the Ruderman-Kittel model, $J_{\text{ex}} = 0.2 \cdot 10^{-21}\text{erg}$, was found to be consistent with the measured value of $\omega_{osc}$.

(ii) As shown on Fig.2b, $^{207}T_2$ changes within the non-uniformly broadened spectra. The arrows point to the operating frequencies. The data can be fitted with the following expression $^{207}T_2(\nu)^{-1}_{\text{exp}} \sim ^{207}K^\alpha(\nu)$ where $\alpha = 1.0 - 1.3$ for $x < 0.2$. The Knight shift $^{207}K_s(x)$ for a fixed $x$, was defined as follows. We have assumed that the chemical part of the total shift does not change with $x$ since the valence state of lead is fixed (Pb$^{+IV}$). Thus, we write :

$$^{207}K_s(x) = \left\{ ^{207}K(x) - ^{207}K(x = 0.36) \right\} = \frac{1}{\mu_B} \frac{^{207}H_{hf}}{^{207}H_{hf}} \chi_{s,\text{loc}}$$

($^{207}H_{hf}$ is hyperfine magnetic field arisen due to hyperfine interaction with conducting electrons, which spin density near the given atom can be characterized by local spin susceptibility $\chi_{s,\text{loc}}$.

(iii) The $T_2(\nu)$ values decrease sharply with increasing $x$ on approaching the metal-semiconductor transition.

Taking into account the variation of $T_2$ within a spectrum, we have restored the real $^{207}$Pb NMR line shape in the following way (Fig.2c): the intensity of echo signals measured at each frequency, $\nu$, with $\tau_{del} = 10\mu$s was multiplied by the factor $\exp(2\tau_{del}/T_2(\nu))$.

Comparing the restored line shapes ($\tau_{del} = 0$) to the spectra measured with $\tau_{del} = 10\mu$s, one may see that line B corresponding to $\text{BaPbO}_3$ is still present in $x = 0.09$ and 0.12 compounds. Nevertheless, the corresponding Knight shift shows a small increase as $x$ increases. Line B is located on a low- frequency edge of a broad line (line C). Line C shifts toward higher frequency as $x$ increases.

On the SCR boundary, for $x = 0.12$, the resulting spectrum has the best resolved structure (Fig.2c) since line B and C have more or less the same weight. For $x ≥ 0.15$, mainly line C is present, line B has almost disappeared. The dominant intensity of line C in SCR corresponds to $^{207}K_s > 1.5\%$.

Thus, substituting Bi in $\text{BaPbO}_3$ produces a large broadening of the spectra due to a distribution of the Knight shifts. The broadening is accompanied by a distribution of $^{207}T_2^{-1}(\nu)$ and $^{207}T_1^{-1}(\nu) \sim ^{207}K^2(\nu)$. It reveals a non uniform ($\nu = 0$) distribution of the carrier density “depending” on the local environment of the lead atoms.

Let us focus on the non superconducting metallic compounds, $x < 0.12$. Since $x$ is rather small, it is reasonable to assume a random distribution for Bi ions in the Pb-sites. As shown on Fig.3, the measured relative intensity of line B ($^{207}\text{Int}_B$) decreases while the width of line C ($\Delta K_x$) increases with increasing $x$. In parallel, for line C, the relative intensity as well as the shift of the center of gravity (Fig.2c) increases as the Bi concentration increases. Thus, Pb atoms located in an area around Bi experience a high local spin susceptibility $\chi_{s,\text{loc}}$. The characteristic radius of this area can be estimated on the assumption of a binomial distribution $P_1(x)$ which valid only for Bi-diluted oxides. On Fig.3, the upper curve $P_1(x) = (1 - x)^6$ corresponds to the fraction of Pb having no Bi atoms in the nearest cation shell. The bottom curve $P_2(x) = (1 - x)^{18}$ is the fraction of Pb having no Bi atoms in both nearest and the next nearest cation shells. The experimental data $^{207}\text{Int}_B$ are well situated between these two curves, $P_1(x)$ and $P_2(x)$, which means that the radius of the area with high $\chi_{s,\text{loc}}$ around Bi, line C being attributed to Pb atoms in these areas, does not exceed 1-2 lattice constants. A steeper decrease of $^{207}\text{Int}_B$ occurs...
different magnetic fields allowed us to determine with a reasonable accuracy the components $^{17}K_{iso}$, $^{17}K_{ax}$ of the magnetic shift and $\nu Q$, $\eta$ the EFG tensor. $\nu Q$, $\eta$ are related to the corresponding Cartesian components $V_{ii}$ of electric field gradient:

$$\nu Q = \frac{3e^2Q}{2I(2I-1)hV_{zz}}, \eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

with $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$ (2)

For both parent compounds, BaPbO$_3$ and BaBiO$_3$, all the oxygen sites are equivalent since the corresponding spectrum can be described with a single set of magnetic shift and EFG. The two-peak line shape is due to the second order quadrupole effect on a powder spectrum (see BaPbO$_3$ on Fig.4). The symmetry of the EFG tensor is almost axial. It should be noted that the values of $K_{iso}$ and $\eta$ listed in Table 1 are consistent with the results reported in Ref. [21].

Magnetic and charge equivalence of the oxygen sites is destroyed in the intermediate metallic compositions for which spectra show a rather complex structure (Fig.4), each peak or shoulder having its own dependence on $\tau_{del}$ and on the repetition time. The intensity of the high frequency part of the spectrum grows with increasing x, correspondingly $(T_2)^{-1}$ is also larger. These changes evidence that in the Bi-containing oxides there is a distribution of the fluctuating hyperfine magnetic fields responsible for processes of spin-lattice and spin-spin relaxation at the oxygen sites.

The less distorted line shapes are obtained for the shortest $\tau_{del}$ value, $\tau_{del} = 35\mu s < (17T_2)_{min} \approx 600\mu s$. The powder spectra of the central transition measured at $B_0 = 12T$ is rather well resolved in the Bi-diluted oxides, $x = 0.09$ (Fig.4). This spectrum is the superposition of three lines, the deconvolution is shown in Fig.5a.

All the simulated lines are broadened by convoluting with a Gaussian function. The function is specified in terms of an isotropic shift and quadrupole frequency and its width at a half of height $(\delta K_{iso})$ or $(\delta \nu Q)$. The EFG parameters were deduced for each line from the central line measured at low field, $B_0 = 2T$ (Fig.5) and the satellite lines (Fig.6). The calculated spectra are shown by dotted lines in Fig.5 and the relevant shift and EFG parameters are listed in Table 1. For all the metallic compositions the spectra can be simulated with the same three lines, by varying the relative intensities of these lines. Only $\eta$ was adjusted for line 3 with the largest magnetic shift. These three lines correspond to three oxygen sites differing mainly by their magnetic hyperfine fields.

In order to understand the origin of the three lines we have analyzed the variation of the spectra as a function of $x$. The tensor components of line 1, $^{17}K_{iso}$, $^{17}K_{ax}$, $\nu Q$ and $\eta$ are very close to those obtained for pure BaPbO$_3$. Its intensity decreases as Bi concentration increases. Line 2 and 3 appear only when Bi cations are present. Considering the measured relative intensities, $^{17}I_m(x)$, plotted on Fig.7, it is quite natural to assume that line 1 originates from oxygen with no Bi in the nearest and next

![FIG. 4: $^{17}$O NMR spectra (transition $m = -\frac{1}{2} \leftrightarrow \frac{1}{2}$) measured at room temperature in BaPb$_{1-x}$Bi$_x$O$_3$ by spin echo technique with different $\tau_{del}$.

for $x \geq 0.09$. It is interpreted as due to the percolative overlap of the Bi-containing areas expected for $x \geq 0.12$ near the transition to SCR.

In SCR, the increase of the relative intensity of line C (Fig.2c) evidences that most of Pb nuclei are in the sites with high $\chi_{s,loc}$.

$^{207}$Pb NMR spectra were available for measurements up to room temperature only for $x \leq 0.15$. It was found that the line position, the total width at half height $(\Delta K_{s})_{0.5}$ and $T_2$ measured at a given $K_s$ are roughly independent of $T$. Unfortunately on the other end of the studied phase diagram i.e. for $x \leq 0.25$, no echo signal was detected in the range of $^{207}K_s > 0.5\%$, probably due to very short $^{207}T_2 < 1\mu s$.

B. $^{17}$O NMR spectra

The oxygen atoms are located at the apex of octahedra with Pb or Bi at the centers. The resonance frequency of $^{17}$O NMR-probe is determined by both the hyperfine magnetic interaction and the quadrupolar interaction.

The $^{17}$O central lines (transition $m_L = -\frac{1}{2} \leftrightarrow \frac{1}{2}$) measured at room temperature at $B_0 = 12T$ are presented in Fig.4. The satellite lines corresponding to the transitions $m_L = \pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ were also measured (Fig.6). Simulation of the central NMR line shapes measured at
nearest shells whereas line 2 and 3 correspond to oxygen with Bi. Furthermore, the function \((1 - x)^{10}\) (fig.7, dashed curve), which represents the binomial probability of the cation configuration without Bi in both, the nearest and the next nearest cation shells around oxygen, fit very well \(17\)\(\text{Int}_1(x)\). Thus line 1 is due to oxygen with no Bi in its two first shells.

The shaded region in Fig.7 shows the range of the expected relative intensity from the binomial model for different Bi-containing configurations of the first cation shell around a given oxygen. The bottom boundary curve, \(2x(1 - x)\) corresponds to the configuration with a single Bi ion in the nearest cation shell whereas the top boundary curve, \(x(2 - x)\), relates to the configuration for which one or two Bi ions are present in the nearest cation shell.
As seen on Fig.7, for small $x$, $x < 0.1$, $^{17}Int_3(x)$ is well described in our model. Thus line 3 with the largest shift can be attributed to oxygen with at least one Bi as nearest neighbor.

The small deviation of $^{17}Int_3(x)$ from the binomial predictions for superconducting oxides ($x > 0.1$) is believed to originate from the overlapping of the areas with the Bi stimulated high electron density. In the overlapped areas the Bi-Bi distance is less than two lattice constants and the foregoing simple binomial approach becomes invalid in SCR. It should be added that the reduction of the EFG symmetry for line 3 (see $\eta$ on Table 1) is in favor with the suggested assignment.

Line 2 dominates in SCR and its intensity reaches a maximum around $x = x(T_{c,max})$ followed by a monotonic decrease in going towards the semiconducting compositions. This line might be attributed to oxygen with Bi ions only located in the second cation shell. The probability of this cation configuration, $(1 - x)^2(1 - (1 - x))^3$, is represented by the dotted line in Fig.7. As it can be seen $^{17}Int_2(x)$ is well described in our model for $x < 0.1$.

The increase of the magnetic shift from line 1 to 3 and the larger $(T_2)^{-1}$ of line 3 have to be put in parallel with the increase of the shift of $^{207}$Pb NMR spectra as the Bi content increases (fig. 2c). As for Pb results, this demonstrates that the random substitution of Pb by Bi in BaPbO$_3$ changes the electron density within two first cation shells.

C. The average Knight shift of $^{207}$Pb and $^{17}$O vs x

Pb NMR line is broadened and shifted mainly due to the distribution of the Knight shift $^{207}K_s$. The average Knight shift $<^{207}K_s>$ is defined as the first moment of the inhomogeneously broadened lines $^{207}g(\nu)$ shown in Fig.2c

$$<^{207}K_s> = \frac{<\nu - \nu_0(x = 0.36)>}{\nu_0(x = 0.36)}$$

$$= \frac{1}{\nu_0} \int (\nu - \nu_0) g(\nu) d\nu$$  \hspace{1cm} (3)

$<^{207}K_s>$ is proportional to the uniform part of the spin susceptibility $\chi_s(q = 0)$.

$$\frac{\mu_B}{^{207}H_{hf}} <^{207}K_s> = \chi_s(q = 0) = \frac{2\mu_B^2 N(E_F)}{1 - J N(E_F)}$$  \hspace{1cm} (4)

where $N(E_F)$ is the bare density of states (DOS) at the Fermi level. As seen on Fig.8, $<^{207}K_s>$ sharply increases at the boundary of SCR. It is rather well scaled with the dependence of the electronic thermal capacity coefficient $\gamma_{el} \sim N(E_F)(1 + \lambda)$ on $x$. $\gamma_{el}$ probes the bare DOS multiplied by the mass enhancement factor $(1 + \lambda)$. The electron-phonon coupling constant was estimated in Ref. [29] and $\lambda$ was found to increase in going towards SCR. This leads to a more slender $x$ variation of $N(E_F)$ when estimated from the heat capacity data as compared to the estimation from the Knight shift data. One may assume that ferromagnetic fluctuations in the conduction band increases and the increase of $\chi_s(q = 0)$ occurs due to nonvanishing Stoner’s enhancement factor $JN(E_F)$.

Let us now consider the average NMR isotropic shift of oxygen $<^{17}K_{iso}>$. It is defined by an expression similar to (4) where $^{17}g(\nu)$ is the sum of three Gaussian lines with relative intensity $(^{17}Int)_i$, and magnetic shift $(^{17}K_{iso})_i$ corresponding to line 1, 2 and 3 respectively. The respective widths, $(\delta K_{iso})_i$, of the Gaussian lines were deduced from simulation. The thermal behaviour of $<^{17}K_{iso}>$ down to $T = 20K$ is displayed in Fig.9. For $x < 0.27$, $<^{17}K_{iso}>$ is temperature independent. For $x = 0.33$, i.e. near the transition to semiconducting state, a gradual decrease of $<^{17}K>$ with decreasing temperature is found. For this sample the static magnetic susceptibility is also T-dependent. In the range of $T = 80 - 300K$ the measured slope $(\Delta \chi/\Delta T)_{T=0.67} = 4.5 \times 10^{-11}$emu/gr·K is consistent with the data reported in [28].

Both observations are in favor of the opening of a gap near $E_F$ when approaching to the metal-semiconductor transition.

The total magnetic shift of $^{17}$O NMR line is the sum of two contributions:

$$<^{17}K>(x, T) = <^{17}\delta>(x) + <^{17}K_s>(x, T)$$

$$<^{17}\delta> + \frac{1}{\mu_B} H_{hf}\chi_s(q = 0)$$  \hspace{1cm} (5)

where $^{17}K_s$ is the Knight shift and the other shift contributions are summarized as ”chemical shift” $^{17}\delta$. For light atoms like oxygen both terms in (6) are comparable in magnitude.
FIG. 9: Temperature dependence of the average NMR shift of oxygen \( <^{17} K > \) in BaPb\(_1-x\)Bi\(_2\)O\(_3\): ■ \( x=0.09 \), ▼ \( x=-0.21 \), □ \( x=0.27 \), △ \( x=-0.33 \). Inset shows \( <^{17} K > \) vs magnetic susceptibility \( \chi_m \) of the sample \( x=0.33 \).

For BaPbO\(_3\) we have estimated \( ^{17}K_s(x = 0) = 130(20)ppm \) starting from the ratio of \( ^{207}\)Pb and \( ^{17}\)O shifts and using eq. (1), (4) and (5). The ratio of corresponding hyperfine fields ( \( ^{207}H_{hf}/^{17}H_{hf} = 50(5) \) ) was estimated by taking into consideration the spin-lattice relaxation rate data of \( ^{17}\)O and \( ^{207}\)Pb\(_{1-x}\)Bi\(_x\)O\(_3\). The deduced \( ^{17}\delta \) value is \( ^{17}\delta (x = 0) = 220(20)ppm \). Assuming that \( ^{207}H_{hf}/^{17}H_{hf} \) is the same in all the metallic samples, we have deduced the \( x \) dependence of \( <^{17} K_s > \) and \( <^{17} \delta > \) using \( <^{207} K_s(x) > \) data up to \( x=0.25 \) (see Table 1). We find that \( <^{17} \delta > \) is constant within the error bar.

As shown in the previous section the oxygen with no Bi as the nearest neighbor give the main contribution to the \( ^{17}\)O NMR line in superconducting samples. Thus one may conclude that no additional paramagnetic (other than \( \chi_{Pauli} \)) contribution to \( ^{17}\delta \) (line-2) appears at these oxygen sites.

At low temperatures \( <^{17} K_s > \) passes through a maximum and then decreases for \( x = 0.33 \). Assuming that for \( x = 0.33 \) \( <^{17} \delta > = 200 \) ppm, the average Knight shift is about \( <^{17} K_s(x = 0.33) >= 300 \) ppm and the corresponding bare DOS as \( N(E_F)_{NMR} = \frac{<^{17}K_s>}{2π^2 H_{hf}} = 0.16(eV \cdot spin)^{-1} \). It should be noted that \( N(E_F)_{NMR} \) exceeds more than twice \( N(E_F) \), evaluated from the electronic thermal capacity coefficient \( \gamma_{el} \) in Ref. \( 2 \) for \( x = 0.30 \), which chemical composition is nearly the same as in BaPb\(_{0.67}Bi_{0.33}O\(_{3}\).\)

IV. SUMMARY

The NMR spectra of \( ^{207}\)Pb and \( ^{17}\)O were measured as a function of temperature and \( x \) in the metallic phase and in the superconducting BaPb\(_1-x\)Bi\(_x\)O\(_3\) \( (0 \leq x \leq 0.33) \). Magnetic shift and broadening of the spectra were analyzed. It was shown that powder patterns of the spectra are modified due to distribution of the Knight shift. The deconvolution of inhomogeneously broadened spectra by 3 lines has allowed to reveal a systematic evolution of the separate lines intensities with the Bi concentration. Each of these lines was attributed to NMR probe with a certain configuration of the neighboring and the next neighboring Pb(Bi) cation shells.

It was established that in the Bi-diluted oxides the areas with increased density of mobile carriers arise around the Bi atoms. The characteristic size of these areas does not exceed two lattice constants. The percolative overlapping of these areas is expected at higher Bi concentrations in superconducting BPBO compositions.

The temperature dependence of magnetic shift for \( ^{17}\)O NMR lines gives an evidence of the gap at \( E_F \) in the metal BPBO oxides near the metal to semiconductor transition.

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* Corresponding author: Dr. S. Verkhovskii, Institute of Metal Physics, UB RAS, Kovalevskaya str., 18, Ekaterinburg 620219, Russia; Fax: + 7 343 2 - 745244; E-mail: Verkhovskii@imp.uran.ru

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TABLE I: $^{17}$O NMR line parameters (for detail see text and Fig.5)

| $^{17}K_{iso}$, ppm | $x$ | 0.0 | 0.03 | 0.09 | 0.15 | 0.21 | 0.27 | 0.33 |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| line 1              |     |     |     |-----|     |-----|     |     |
| line 2              |     |     |     |-----| 510(15)| 120(20)|   |     |
| line 3              |     |     |     |-----|     |     |     |     |
| $^{17}K_{ax}$, ppm  | line 1 |     |     |-----|     |     |     |     |
| line 2              |     |     |     |-----|     |     |     |     |
| line 3              |     |     |     |-----|     |     |     |     |
| $\delta K_{iso}$, ppm | line 1 |     |     |-----|     |     |     |     |
| line 2              |     |     |     |-----|     |     |     |     |
| line 3              |     |     |     |-----|     |     |     |     |
| $\delta K_{ax}$, ppm | line 1 |     |     |-----|     |     |     |     |
| line 2              |     |     |     |-----|     |     |     |     |
| line 3              |     |     |     |-----|     |     |     |     |
| $\nu_{Q}$ MHz      | line 1 |     |     |-----| 1.13(3)| 0.05(3)|   |     |
| line 2              |     |     |     |-----| 1.15(3)| 0.05(3)|   |     |
| line 3              |     |     |     |-----| 1.1(1)| 0.1(1)|   |     |
| $\eta$             | line 1 |     |     |-----|     |     |     |     |
| line 2              |     |     |     |-----| 0.05| 0.015| 0.2|     |
| line 3              |     |     |     |-----|     |     |     |     |
| Relative            | line 1 | 1.0| 0.81| 0.41| 0.12| 0.3| 0.35| 0.5 |
| intensity           | line 2 | 0 | 0.14| 0.43| 0.39| 0.7| 0.65| 0.6 |
| line 3              |     |     |     |-----|     |     |     |     |
| $<K_{iso}>$, ppm    | 300K | 350(10)| 390(10)| 480(20)| 520(20)| 570(20)| 580(20)| 590(20)|
| 20K                | 350(10)|     | 500(20)|     | 560(20)| 560(20)| 500(20)|     |