Low temperature properties of lead dioxide: NMR study and calculations of zone structure

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Abstract

The local magnetic fields on the ^{207}Pb nuclei have been measured by NMR method on the lead dioxide having the rutile structure (β-PbO_2) at the temperatures of $20K$ and 290 K. It was shown that both the local fields quantities and their temperature behavior correspond to the Knight mechanism of NMR spectra shifts in metals. Zone structure calculations have also been done accounting for the relativistic correlations. The results obtained were used as a basis for conclusions about nature of metallic conductivity of the dioxide studied.

Key words: Knight shift; lead dioxide

Our preliminary data on the NMR spectra of lead dioxide were published earlier [1]. It was shown that the samples were characterized by inhomogeneous distribution of the oxygen ion vacancy, which resulted in a number of oxides with very similar content none of which was equal to the stoichiometric one.

The ^{207}Pb NMR spectra were recorded with Bruker spectrometer at 290 K and 20 K in the field $B_0 = 9.1$ T. Each spectrum was a sum of 15 subspectra, obtained at equally distanced frequencies (with the step equal to 80 kHz). The ^{207}Pb NMR spectra of β-PbO_2 were shifted in the direction of magnetic field B which was lower than the B_0 value for ^{207}Pb NMR signal of the solid lead nitrate $Pb(NO_3)_2$. The shift value $(B - B_0)$ corresponded to an additional magnetic field induced on the nuclei ^{207}Pb. The local magnetic field changed proportionally to the external field B, so its quantity may be characterized by of the relative shift value of the NMR signal peak: $\sigma = (B - B_0)/B_0$. We obtained the following values: $\sigma = -(0.850 \pm 0.002)$ % (at 290 K), and $\sigma = -(0.904 \pm 0.002)$ % (at 20 K).

These values are close to σ = - 0.82% for the metallic substance $BaPbO_3$ [2] and to the value σ = - 1.345% (at 100 K) for the superconducting $Ba(Pb_{0.85}Bi_{0.15})O_3$ [2]. Thus, judging by the shift values, the β-$PbO_2$was really an oxide with expressed metallic properties. In this case, the appearance of induced magnetic fields and the related shifts of NMR spectra was caused by the Knight mechanism [2, 3]. Especially notable is a strong temperature dependence of the Knight shift of $\beta - PbO_2$. This phenomenon is likely connected with the increase of electroconductivity which is characterictically observed in common metals with the decrease in temperature.

The calculation of $\beta - PbO_2$ bond structure was made with the computer program ADF-Band (The Netherlands) utilizing the density functional theory [4]. Exchange and correlative interactions were approximated with the functional VWN [5]. The relativistic effects (both scalar and spin-orbital interactions) were taken into account in the zero order approximation ZORA [6]. Slater orbitals (both relativistic and non-relativistic) were used as basic wave functions; the Pb atom was represented by $5d$, $6s$, $6p$, and $6d$ orbitals, and the O atom, by $2s$ and $2p$.

When we took into account the relativistic corrections, we fond that the Fermi level was located inside the filled zone, but close to its upper boundary.

Speaking of the experimental data, the large value of the ^{207}Pb NMR spectrum shift in PbO_2 and its sub-

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stantial temperature dependence may be explained using the model of strong electron-nuclear interaction of ^{207}Pb nuclei with conducting electrons in compounds with the metallic character of bond [7, 8]. The experimental values of PbO_2shifts are comparable (in the order of magnitude) with the Knight shifts of the metallic lead ^{207}Pb NMR [9]: $\sigma_K = 1.465$ % (290 K), and $\sigma_K = 1.400$ % (extrapolation of the [9] data to 20 K). One can see that the metallic Pb and its dioxide PbO_2 are characterized by the opposite signs of Knight shift temperature dependence coefficients: in the former case the shift value decreases with the decrease of temperature, and in the latter, it increases. This difference may be explained by the presence in both Pb and PbO_2 of two terms with opposite signs [8, 10, 11]. The first term is the direct contact part related to s-state Fermi electrons. The second one (the so called polarization part) is related to the exchange interaction of the unfilled p-shell electrons with filled inner s-shells and their partial polarization, which leads to the appearance of the additional contact hyperfine field on the nucleus (with the opposite sign).

As to the nature of lead dioxide metallic conductivity, the following observations may be in order. In the 1960s, as part of his metal bond magnetism theory, J. Friedel developed the concept of virtual electronic levels occurring in the conducting zone due to fluctuations [12]. The peculiarities of bond structure, and (it must be emphasized particularly) inhomogeneous distribution of charge density in the substance, make it quite likely that these types of levels may occur in the empty conductive bond of the lead dioxide. The resonance smearing of levels into a narrow bond provides, in the normal metals, for an additional (and in the lead dioxide, for the primary) conductivity. Note also that the analysis of experimental data leads us to the conclusion that both 6p and 5d electrons of lead filled shells may be involved in the formation of the virtual electronic levels.

This study was supported by RFBR (grant 02-03-32319).

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