

## Spin-Singlet Small Bipolarons in Nb-Doped BaTiO<sub>3</sub>

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The magnetic susceptibility and the electrical resistivity of *n*-type BaTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> have been measured over a wide temperature range. It is found that, for  $0 < x < 0.2$ , dopant electrons form immobile spin-singlet small bipolarons with binding energy around 110 meV. For  $x = 0.2$ , a maximum in the electrical resistivity around 15 K indicates a crossover from band to hopping transport of the charge carriers, a phenomenon expected but rarely observed in real polaronic systems.

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The theoretical treatment of itinerant carriers interacting with a strongly polarizable lattice has been conducted for over 50 years, resulting in a variety of different models. Depending on the degree of electron-lattice interaction, these models can be roughly divided into two main groups. The first [1,2] treats the electron as a Bloch-wave-like delocalized particle called a Fröhlich or large polaron. The second [3,4] assumes an extreme localization of the itinerant electron within one or several lattice sites (i.e., a small polaron, SP) accompanied by a strong local lattice deformation. It is expected that under certain conditions, polarons can pair to form large or small bipolarons, BP [5,6]. Although not without controversy [7], several authors suggest [6] that Bose-Einstein condensation of bipolarons may result in high- $T_c$  superconductivity.

Evidence of a strong electron-lattice interaction has been accumulating for ATiO<sub>3</sub>, where  $A = \text{Ba}$  or  $\text{Sr}$  [8,9]. These are textbook examples of crystals having a simple perovskite structure and high static dielectric constant furnished by a soft phonon mode. Stoichiometric ATiO<sub>3</sub> are band gap insulators. Donor doping or reduction in an oxygen-deficient atmosphere results in an *n*-type material with unconventional electronic conductivity where the carriers move within a very soft and deformable lattice. In *n*-type SrTiO<sub>3</sub>, the electron-lattice interaction is not strong enough to cause the localization of the itinerant electrons which consequently form large polarons. As a result, *n*-type SrTiO<sub>3</sub> shows metallic conductivity with an enhanced effective electron mass  $m^*$  of  $6m_e$  to  $14m_e$  [10,11]. It has been argued that, at low temperatures, large polarons in *n*-type SrTiO<sub>3</sub> condense into the large BPs responsible for superconductivity below 0.6 K [11].

The lattice constant of cubic BaTiO<sub>3</sub> ( $a = 0.4005$  nm) is 2.5% larger than that of SrTiO<sub>3</sub> ( $a = 0.3905$  nm). This small increase in  $a$  causes a dramatic difference in the electronic properties of the two compounds. Unlike *n*-type SrTiO<sub>3</sub>, the conductivity of *n*-type BaTiO<sub>3</sub> shows insulating behavior with the low conductivity attributed to the thermally activated hopping of strongly localized electrons (i.e., small polarons) between neighboring Ti sites. Gerthsen *et al.* [12] explained the midinfrared reflectance of *n*-type BaTiO<sub>3</sub> in terms of the SP absorption model. In

accord with the hopping transport of SPs, Bursian *et al.* [13] found that the Seebeck coefficient of weakly doped *n*-type BaTiO<sub>3</sub> is temperature independent above 300 K. Direct evidence of the self-trapped Ti<sup>3+</sup> SP was provided by ESR studies of acceptor depleted BaTiO<sub>3</sub> [14]. Nevertheless, the SP interpretation of the electronic properties of BaTiO<sub>3</sub> is far from uncontroversial. Two major points of disagreement are the similarity in the Hall and drift mobilities ( $\mu_{\text{Hall}} \approx \mu_{\text{drift}} \approx 0.2$  cm<sup>2</sup>/Vs at 300 K), which, according to the SP model, should satisfy  $\mu_{\text{Hall}} \gg \mu_{\text{drift}}$  [15], and the large difference between the optical and thermal activation energies ( $E_{\text{op}} = 500\text{--}600$  meV,  $E_{\text{th}} = 23$  meV) of the proposed SPs that should satisfy  $E_{\text{op}} = 4E_{\text{th}}$  [16].

In our opinion, the polaronic approach to understanding the unusual properties of *n*-type BaTiO<sub>3</sub> requires that the possibility of electron pairing be taken into account. The coupling of electrons into Anderson-type *on-site* spin-singlet Ti<sup>2+</sup> small bipolarons according to  $\text{Ti}^{4+} + 2e^- \rightarrow \text{Ti}^{2+}$  was first postulated by Moizhes and Suprun [17]. Later, the idea of BPs in BaTiO<sub>3</sub> was supported by Lenjer and co-workers [9], who observed an unexpected increase in the Ti<sup>3+</sup> ESR signal with temperature. This observation led them to suggest that, due to the high correlation energy that sets the energy cost for a double occupancy of the Ti<sup>2+</sup> ion, the symmetry of the BP is rather of the *intersite*, i.e., Heitler-London type, where the electron pair is localized at two neighboring Ti<sup>3+</sup> ions according to  $2\text{Ti}^{4+} + 2e^- \rightarrow 2\text{Ti}^{3+}$ .

The central question addressed in this Letter is whether the Ti<sup>3+</sup>  $S = \frac{1}{2}$  small polarons in *n*-type BaTiO<sub>3</sub> remain isolated at  $T = 0$  K or if they pair into spin-singlet  $S = 0$  bipolarons. We also report on the physical properties of the BPs in *n*-type BaTiO<sub>3</sub>, as revealed by magnetic and electrical measurements.

Polycrystalline BaTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> samples with  $0 \leq x \leq 0.2$  were prepared by solid state reaction from high purity 99.99% BaCO<sub>3</sub>, TiO<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub>. Sintering was performed in forming gas (3%H<sub>2</sub> + 97%N<sub>2</sub>) to ensure electronic rather than cation vacancy compensation of the Nb dopant [18]. Phase purity of the ceramics was confirmed by powder x-ray diffraction and energy dispersive x-ray mi-

croanalysis with no evidence of secondary phases up to  $x = 0.2$ .

Assuming strong localization of excess electrons on isolated  $\text{Ti}^{3+}$  ions down to 0 K (SP ground state), the magnetic susceptibility should decrease with temperature in accordance with the Curie law,

$$\chi_{\text{para}} = \frac{N_A p^2 \mu_B^2 c_P}{3k_B T}, \quad (1)$$

where  $N_A$  is the Avogadro number,  $p$  is the effective magnetic moment in Bohr magnetons ( $\mu_B$ ),  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $c_P$  is the concentration of small polarons. Figure 1 shows the temperature dependence of the molar magnetic susceptibility,  $\chi_M$ , of the  $\text{BaTi}_{1-x}\text{Nb}_x\text{O}_3$  ceramics in the 2–800 K temperature range. It is obvious that the  $\chi_M(T)$  data do not support a simple SP scenario. The observed anomalous increase in  $\chi_M$  at intermediate temperatures is associated with the breaking up of spin-singlet BPs. An overall increase in  $\chi_M$  with dopant concentration is attributed to the formation of the BP band with associated van Vleck paramagnetism. To fit the data we apply Emin's formalism [19] for dissociation of small BPs in a weak magnetic field ( $g\mu_B B \ll 2k_B T$ ). According to Emin, the concentration of SPs,  $c_P$ , produced by thermal dissociation of BPs is given by

$$c_P = \frac{1 - (1-x)\sqrt{1 + [x(2-x)/(1-x)^2]e^{\varepsilon_b/k_B T}}}{1 - e^{\varepsilon_b/k_B T}}, \quad (2)$$

where  $x$  is the concentration of the  $\text{Nb}^{5+}$  dopant and  $\varepsilon_b$  is the BP binding energy, i.e., the energy required to split the BP into two SPs. The data in Fig. 1 were fitted with the general formula

$$\chi_M = \chi_{\text{dia}} + \chi_{\text{VV}} + \frac{A}{T} + \chi_{\text{para}}, \quad (3)$$

where  $\chi_{\text{dia}} = -2.32 \times 10^{-5} \text{ cm}^3/\text{mol}$  is the diamagnetic

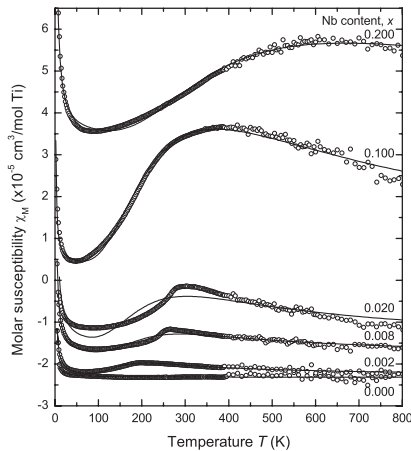


FIG. 1. Magnetic susceptibility per mole of Ti of the  $\text{BaTi}_{1-x}\text{Nb}_x\text{O}_3$  ceramics with  $x = 0, 0.002, 0.008, 0.020, 0.100,$  and  $0.200$ . Solid lines are fits to the data as described in the text.

susceptibility of the undoped, stoichiometric  $\text{BaTiO}_3$ ,  $\chi_{\text{VV}}$  is the temperature independent van Vleck paramagnetic contribution, and  $A$  accounts for impurity-related paramagnetism dominant at  $T < 40$  K.

The van Vleck term is given by

$$\chi_{\text{VV}} = \frac{2N_A x |\langle l|\mu_z|0\rangle|^2}{\Delta}, \quad (4)$$

where  $\langle l|\mu_z|0\rangle$  is a nondiagonal matrix element of the magnetic moment operator connecting the BP ground state 0 with the excited state  $l$  of energy  $\Delta = E_l - E_0$  above the ground state.

The results of the fit are shown as solid lines in Fig. 1. The fitting parameters are summarized in Table I. A somewhat larger value of  $A$  for the  $x = 0.2$  sample is attributed to the partial compensation of the Nb dopant by paramagnetic cation vacancies as we approach the solubility limit of Nb in  $\text{BaTiO}_3$ . In agreement with Eq. (4),  $\chi_{\text{VV}}$  is found to scale linearly with dopant concentration. Good fits were obtained for  $x = 0, 0.002, 0.1,$  and  $0.2$  and somewhat worse fits for  $x = 0.008$  and  $0.02$ . We can explain the poor fit at intermediate dopant concentrations since, while fitting the data, we have assumed a constant  $\varepsilon_b$  and  $\chi_{\text{VV}}$  for the entire temperature range. It is known, however, that undoped  $\text{BaTiO}_3$  exists in four crystallographic forms [20]: rhombohedral at  $T < 200$  K, orthorhombic at  $200 \text{ K} < T < 270$  K, tetragonal at  $270 \text{ K} < T < 393$  K, and cubic at  $393 \text{ K} < T < 1670$  K. Since both  $\varepsilon_b$  and  $\chi_{\text{VV}}$  depend on the crystal symmetry, the use of single values of  $\varepsilon_b$  and  $\chi_{\text{VV}}$  for  $x = 0.008$  and  $0.02$  gives only marginally satisfactory results. At the lowest dopant concentration ( $x = 0.002$ ), 70% of the BPs are already dissociated into SPs at 200 K, i.e., fully within the rhombohedral phase. As a result, this fit is good in spite of the single values of  $\varepsilon_b$  and  $\chi_{\text{VV}}$  used. Doping with Nb results in a significant lowering of the phase transition temperatures in  $\text{BaTiO}_3$  [21]. Indeed, low-temperature x-ray analysis of the  $x \geq 0.1$  samples confirmed that they remain cubic down to at least 20 K. Hence, the use of single values of  $\varepsilon_b$  and  $\chi_{\text{VV}}$  produces a good fit also in these cases. The data show that in the doping range covering 2 orders of magnitude, the bipolaron binding energy is of the order of 110 meV. For the most highly doped sample ( $x = 0.2$ ), the bipolaron binding energy (172 meV) is found to be rather high. This may be due to the solubility limit of donor atoms and/or BP overcrowding effects.

TABLE I. Fitting parameters for  $\chi_M$  of  $\text{BaTi}_{1-x}\text{Nb}_x\text{O}_3$ .

$x$	$\chi_{\text{VV}}$ [ $10^5 \text{ cm}^3/\text{mol}$ ]	$A$ [ $10^5 \text{ cm}^3 \text{ K}/\text{mol}$ ]	$\varepsilon_b$ [meV]	$p$
0.000	0	2.16	...	...
0.002	0.02	5.73	106	0.57
0.008	0.47	11.73	122	0.46
0.020	0.73	16.64	111	0.46
0.100	2.68	5.96	105	0.42
0.200	5.69	22.5	172	0.36

One might argue, however, that the BP interpretation of the  $\chi_M$  anomaly is not convincing enough, and that thermal activation of intrinsic or extrinsic lattice defects may generate similar effects. Let us address this crucial argument in detail. Since no  $\chi_M$  anomaly is observed in undoped, stoichiometric BaTiO<sub>3</sub>, the possibility of the  $S = 0 \rightarrow S = \frac{1}{2}$  activation of any supposed extrinsic impurities can be ruled out. According to the point defect chemistry of BaTiO<sub>3</sub>, the Nb<sup>5+</sup> dopant is compensated by barium or titanium vacancies at high oxygen partial pressures ( $P_{O_2}$ ) and by electrons at low  $P_{O_2}$  [18]. Since the samples were prepared at low  $P_{O_2}$ , the concentration of cation vacancies is negligible. However, even if a small amount of cation vacancies were still present in the heavily doped samples, their thermal activation energy is at least 5 times higher than  $\varepsilon_b$  [18]. It is quite possible that oxygen vacancies ( $V_O$ ) are present in the samples. According to recent calculations [22], these vacancies will form a  $[\text{Ti}^{3+} - V_O - \text{Ti}^{3+}]$  neutral complex defect. In fact, the  $[\text{Ti}^{3+} - V_O - \text{Ti}^{3+}]$  complex is nothing other than the small BP bound to the oxygen vacancy, although in this case the electrons are localized on the Ti  $3z^2 - r^2$  orbitals [23]. Activation of this defect according to  $[\text{Ti}^{3+} - V_O - \text{Ti}^{3+}] \rightarrow [\text{Ti}^{3+} - V_O] + \text{Ti}^{3+}$  may indeed cause a  $\chi_M$  anomaly similar to that observed in Fig. 1. However, donor doping always decreases the concentration of  $V_O$  [18]. Hence one would expect a decrease in the  $\chi_M$  anomaly with increasing doping, which is opposite to what is seen in our results. Finally, we rule out the possibility that the  $\chi_M$  anomaly is associated with a change in the ionization state of Nb<sup>5+</sup> according to  $\text{Nb}^{4+} + \text{Ti}^{4+} \rightarrow \text{Nb}^{5+} + \text{Ti}^{3+}$  since we have confirmed that similar magnetic anomalies occur when electrons are introduced into BaTiO<sub>3</sub> by donors ( $\text{Y}^{3+}$  and  $\text{La}^{3+}$ ) having a stable oxidation state.

Recent studies suggest that magnetic anomalies in several  $3d^1$  titanates including MgTi<sub>2</sub>O<sub>4</sub>, NaTiSi<sub>2</sub>O<sub>6</sub>, and LiTiSi<sub>2</sub>O<sub>6</sub> [24] are associated with the formation of spin-singlet  $\text{Ti}^{3+} - \text{Ti}^{3+}$  pairs. In contrast to the above compounds, the formation of BPs in  $n$ -type BaTiO<sub>3</sub> is not driven by a change in the crystal symmetry, as revealed in the samples with  $x \geq 0.1$ . Most remarkably, pairing of the electrons occurs even for very diluted  $3d^{0+\delta}$  ( $\delta \ll 1$ ) electronic concentrations as in the case of  $x = 0.002$ . In view of the heated debate regarding the possibility of the existence of *mobile* small BPs [7], we have also examined the electronic behavior of  $n$ -type BaTiO<sub>3</sub>. According to the resistivity data shown in Fig. 2, the ground state of  $n$ -type BaTiO<sub>3</sub> is insulating throughout the  $0 < x < 0.2$  doping range [25] and therefore comprises immobile small BPs. The total conductivity can be expressed as a sum of polaronic,  $\sigma_P$ , and bipolaronic,  $\sigma_{BP}$ , conductivities:

$$\sigma = \sigma_P + \sigma_{BP} = ec_P\mu_P + 2e\frac{x-c_P}{2}\mu_{BP}, \quad (5)$$

where  $\mu_P$  and  $\mu_{BP}$  are the drift mobilities of SPs and BPs, respectively. We assume, in accordance with Ref. [19], that for a low doping level the main contribution to  $\sigma$  comes

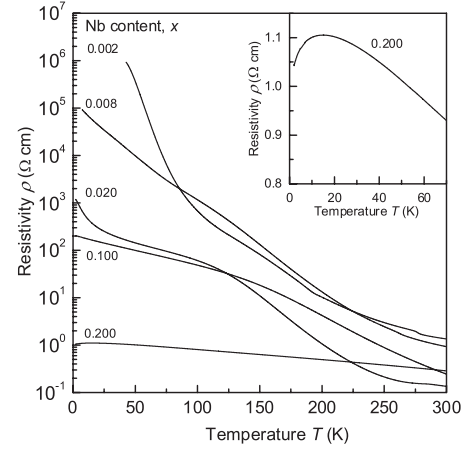


FIG. 2. Electrical resistivity of the BaTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> ceramics with  $x = 0.002, 0.008, 0.020, 0.100,$  and  $0.200$ . The inset highlights the crossover from band to hopping conduction in the  $x = 0.200$  sample.

from the SPs that are formed by thermal dissociation of the BPs and that  $\sigma_{BP}$  is negligible due to the large effective mass and very low mobility of BPs. Then, in the case of nonadiabatic hopping of SPs [26],

$$\sigma \approx ec_P\mu_P \propto \frac{1}{T^{1.5}} \exp\left[-\frac{\varepsilon_b + E_{th}}{k_B T}\right]. \quad (6)$$

Taking  $E_{th} = 23 \text{ meV}$  from Ref. [16] and  $\varepsilon_b$  from Table I, the total activation energy of conductivity,  $\varepsilon_b + E_{th}$ , should be around  $135 \pm 10 \text{ meV}$  at high temperatures, with a slight deviation for the  $x = 0.2$  sample. Indeed the resistivity data confirm that all but the  $x = 0.2$  sample show activated conductivity above  $T \approx 155 \text{ K}$  with an activation energy of around  $135 \text{ meV}$  as shown in Fig. 3. The strong downturn from Arrhenius behavior for  $T < 155 \text{ K}$  is due to an enhancement of the mobility by quantum lattice fluctuations [27]. As the dopant concentration increases, the  $\sigma_{BP}$  contribution can no longer be neglected. In fact, the sample with the highest doping level ( $x = 0.2$ ) shows a strong conductivity enhancement at low temperature, with a maximum in  $\rho$  at  $T = 15 \text{ K}$  as shown in the inset of Fig. 2. According to the SP theory, the resistivity maximum is expected [27] but rarely observed in real polaronic systems [28]. In our case, it is associated with a crossover from the coherent transport of BPs within the bipolaron band below  $15 \text{ K}$  to the incoherent (i.e., hopping) transport of BPs above  $15 \text{ K}$ . We should stress here that this phenomenon is not unique to Nb-doped samples and has also been observed in La-doped BaTiO<sub>3</sub>.

Finally, let us compare the thermal dissociation energy of BPs,  $\varepsilon_b$ , obtained in this work with literature data on the infrared absorption band of  $n$ -type BaTiO<sub>3</sub> centered at  $E_{op} = 500\text{--}600 \text{ meV}$  [26,29]. Optical absorption of BPs involves the splitting of the two electrons and transfer of one of them to the next neighboring site. According to Emin [30], this process would require an energy of  $E_{op} \approx 4\varepsilon_b$ . Taking  $\varepsilon_b$  data for weakly doped samples ( $x < 0.02$ ) from Table I, the optical absorption due to the BPs would

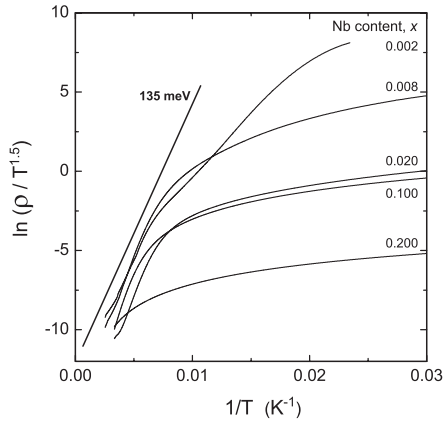


FIG. 3. Arrhenius plot of the resistivity of the  $\text{BaTi}_{1-x}\text{Nb}_x\text{O}_3$  ceramics assuming nonadiabatic hopping of polarons.

produce a band centered at 420–490 meV, which is in reasonable agreement with the literature data. A BP-associated optical absorption is expected to be strongly temperature dependent since the concentration of the BPs decreases with temperature. An alternative source of the midinfrared absorption band in  $n$ -type  $\text{BaTiO}_3$  could be the  $d_{xy} \rightarrow d_{xz}, d_{yz}$  orbital (intraband) excitations. Formation of the SP removes the threefold  $t_{2g}$  orbital degeneracy in  $\text{BaTiO}_3$  due to the  $T_2e$  Jahn-Teller effect. According to ESR data, the energy associated with the orbital excitations within the  $t_{2g}$  band in  $n$ -type  $\text{BaTiO}_3$  is around 400–536 meV [31]. In this case, however, the intensity and the energy maximum of the optical absorption should be temperature independent. Since there are no data on the temperature dependence of the midinfrared band of  $n$ -type  $\text{BaTiO}_3$ , the certain origin of this band remains unresolved.

In conclusion, as revealed by magnetic susceptibility data, “itinerant” electrons in  $\text{BaTi}_{1-x}\text{Nb}_x\text{O}_3$  with  $0 < x < 0.2$  form localized pairs with a spin-singlet ground state. The binding energy of the BPs ranges from 105 to 122 meV depending on the dopant concentration. Electrical resistivity measurements show that, throughout this doping range, the BPs are *immobile*. A crossover from band to hopping transport is manifested by a resistivity maximum at  $T = 15$  K in the most heavily doped ( $x = 0.2$ ) sample investigated. This indicates that at rather high doping concentration, small BPs in  $\text{BaTiO}_3$  become mobile. In a more general perspective, we speculate that  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  play host to the two extreme cases of the bipolaron ground state: the small BP in  $\text{BaTiO}_3$  evolves into a large BP in  $\text{SrTiO}_3$ . Hence,  $\text{BaTiO}_3 - \text{SrTiO}_3$  may become a model system for studies of the physics of small and large BPs as it became a model system for studies of soft mode behavior 50 years ago.

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