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Superconductivity and normal-state magnetic properties of Pr-doped $Ba_{1-x}K_xBiO_3$ single crystals

B Prijamboedi and Hiromoto Uwe

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

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Abstract

Superconductivity and normal-state magnetic properties of Pr-doped $Ba_{1-x}K_xBi_{1-y}$ Pr_yO_3 single crystals have been studied. With Pr doping, T_c decreases rapidly following the Abrikosov–Gor'kov (AG) theory up to Pr concentrations of $y_{tr} \approx 3.5$ and 1.5% for crystals with $x = 0.40$ and 0.53, respectively, but they relax and deviate from the AG-formula curves above y_{tr} before dropping to 0 K. For the normal-state magnetic susceptibility, the Curie–Weiss temperature changes sign from positive to negative values above y_{tr}, where antiferromagnetically coupled Pr magnetic moments blunt the suppression of T_c. The effective magnetic moments of Pr calculated from the observed Curie constants, which are 1.0 μ_B and 1.2 μ_B for $x = 0.40$ and $x = 0.53$, suggest a strong crystal field effect. The Pr doping also enhances the Pauli susceptibility.

1. Introduction

While substitution of magnetic impurities for the constituent atoms in conventional superconductors is known to cause many interesting phenomena, which were sometimes unpredictable before, it brings better understanding on properties or mechanism of the superconductivity. In most cases, the conventional superconductivity is suppressed by the presence of magnetic impurities as described by the Abrikosov–Gor'kov (AG) theory [1] because the spin impurity breaks the time-reversal symmetry. The crystal field effect (CFE) [2, 3] and the Kondo effect [4–6] are, however, found to change the T_c behaviour predicted by the AG theory. In the case of CFE, if the magnetic impurity has a singlet ground state, the T_c suppression rate or the pair-breaking parameter depends on the energy difference between the non-magnetic ground and the magnetic excited states. The large separation leads to the reduction of the T_c suppression rate. In the Kondo effect, the T_c suppression rate is parametrized by the Kondo temperature. In the hole system of an unconventional cuprate superconductor, it is known that non-magnetic impurities suppress the superconductivity more effectively than magnetic impurities. Recent theories [7, 8] indicate that this is the case for a superconductor with d-wave or anisotropic s-wave order parameter.

The $Ba_{1-x}K_xBiO_3$ (BKB) superconductor of cubic perovskite structure [9, 10] has the highest critical temperature (T_c) (≈31 K) among the copper-free oxide superconductors. With

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neither the two-dimensional structure nor the localized magnetic moments, the BKB shares with the cuprate superconductors the characteristics of the unconventional superconductivity such as the linear relation between T_c and n_s/m^* (superconductor carrier density to effective mass ratio) [11]. However, characteristics such as (1) the presence of the charge density wave with the breathing mode distortion of oxygen in the parent compounds of $BaBiO_3$ [12], (2) the oxygen isotope effect for T_c [13], (3) the s-wave order parameter [14] and (4) the ratio of the superconducting gap to T_c of $2\Delta/k_BT_c = 3.5$–4 [15] suggest that the electron–phonon interaction in the weak-coupling limit described by the BCS model is responsible for the pairing mechanism. Therefore, the study of the high T_c mechanism in BKB could help the understanding of the high-T_c phenomena in cuprate or other systems.

The magnetic impurity effect on the BKB, which has not been studied yet to our knowledge, is expected to be novel and interesting, since the BKB has a high T_c value and belongs to a low carrier-density system. The element Pr was chosen for magnetic impurities because the ionic radii of Pr^{4+} (0.78 Å) is close to the average of Bi^{3+} (0.96 Å) and Bi^{5+} (0.74 Å) ionic radii and the properties of Pr in the tetravalent state have been investigated in the insulating perovskite-type crystal of $BaPrO_3$ [16–18]. The magnetic, specific-heat [16], neutron diffraction [17] and optical measurements [18] show that the superexchange interaction leads to the antiferromagnetic stabilization with $T_N = 11.7$ K. The Pr 4f electronic configuration of the Pr^{4+} state has also been observed by an infrared absorption experiment [19]. Although $BaPrO_3$ crystallizes in the orthorhombic symmetry, the Pr ions in the PrO_6 octahedron configuration experience high symmetry, since the Pr–O length along the *ab*-axis (2.225 Å) nearly equals that along the *c*-axis (2.223 Å) [17]. In the cubic phase of BKB, we expect that Pr ions should be substituted for Bi ions with such high symmetry.

However, the synthesis of BKB doped with the rare-earth (RE) elements would usually be difficult, because the high melting point of the RE oxide and the high volatility of potassium conflict for the synthesis. The electrochemical method to prepare Pr-doped BKB single crystals at relatively low temperature allows the synthesis to be successfully carried out. In this paper, two-step suppression of T_c with magnetic impurities and the relation to the normal-state magnetic properties are reported for the Pr-doped BKB single crystals.

2. Experiment

Two series of single crystals of $Ba_{1-x}K_xBi_{1-y}Pr_yO_3$ (BKBP) with K concentrations $x = 0.40$ and 0.53 and Pr concentrations y less than 10% were prepared by the electrochemical method [20, 21]. The starting materials of $Bi2O_3$, Pr_2O_3, KOH and $Ba(OH)_28H_2O$ were placed in a Teflon crucible and melted at temperature of 230 °C with nitrogen flow at 10 cm^3 min^{-1}. The platinum wires were used as the working, counter and reference electrodes. The applied current was 4 mA and the process took 4 days. Single crystals with a typical size of $2 \times 2 \times 2$ mm^3 were selected from the crystal cluster and used for further characterizations and measurements.

The cation compositions of crystals were determined by an electron-probe microanalyser (EPMA) after the surface was polished prior to measurement. The powder x-ray diffraction (XRD) was used to examine the crystals, which can detect the presence of impurities and determine the lattice constant. Si powder was added to the sample during the XRD measurement as reference and the lattice parameter is calculated by the least-squares method. A Quantum Design SQUID magnetometer was used to perform measurements of the superconducting critical temperature T_c as well as the normal-state dc magnetic susceptibility. T_c was determined from the intercept of the slope of the Meissner effect signal with the normal-state extrapolation both in zero-field-cooled (ZFC) and field-cooled (FC) modes at temperature down to 2 K. Magnetic measurements for the Meissner signal were carried out at the field of

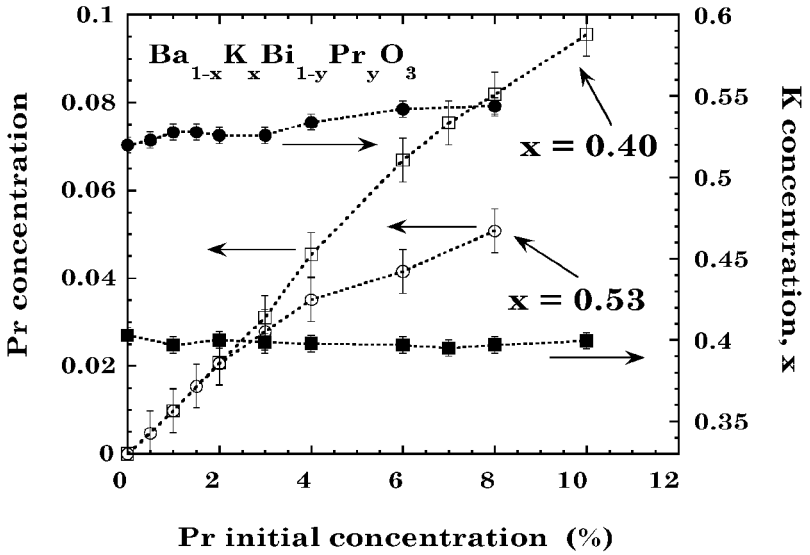

Figure 1. The Pr and K concentration in the single crystal against prepared Pr concentration in the solution.

20 Oe for $y < 4.5\%$ for crystals with $x = 0.40$, and 5 Oe for other cases. The normal-state magnetic susceptibility measurements were performed in the field of 1 T at the temperature range between 5 K and 300 K.

3. Experimental results

Figure 1 shows the Pr and K cation concentrations measured by EPMA as functions of the prepared Pr concentration. In the first series of crystals, the potassium concentration is found to be almost constant ($x = 0.40 \pm 0.005$) and the Pr one has a linear relation with the prepared one. For another series the K concentration shows a slight increase with the prepared Pr one and the average concentration x is 0.53 ± 0.015.

The Pr concentrations in this series ($x = 0.53$) exhibit a tendency of saturation at larger Pr nominal concentrations, which indicates a solubility limit of Pr ions in the BKBP, though the saturation tendency is not observed in BKBP with $x = 0.40$ below $y = 10\%$. The cause of the solubility limit seems to be related to the shorter lattice parameter for $x = 0.53$ than for $x = 0.40$.

A typical XRD spectrum for BKBP with $x = 0.40$ and $y = 8.2\%$ is shown in figure 2(a), which shows a single phase with no impurities such as Pr_2O_3 with the highest melting-point temperature in the raw material. Determined lattice constants are shown in figure 2(b). In the crystal with $x = 0.40$, the lattice parameter for the Pr-doped BKB is slightly lower than for the Pr-free BKB and the Pr-doped values are around 4.280 Å. There is no significant variation of the lattice constant values for the $x = 0.53$ crystals around 4.255 Å. Small changes of the lattice constants indicate that Pr should be in the tetravalent state in accordance with previous results [16–19], because a larger increase of the lattice parameter would be expected for the substitution of Pr^{3+} ions (ionic radius of 1.013 Å) for Bi^{3+} (0.96 Å) or Bi^{5+} (0.74 Å).

The Meissner effect for the crystals is shown in figure 3, in which we can see a single rapid drop of the susceptibility at T_c with an increasing transition width at higher Pr concentrations.

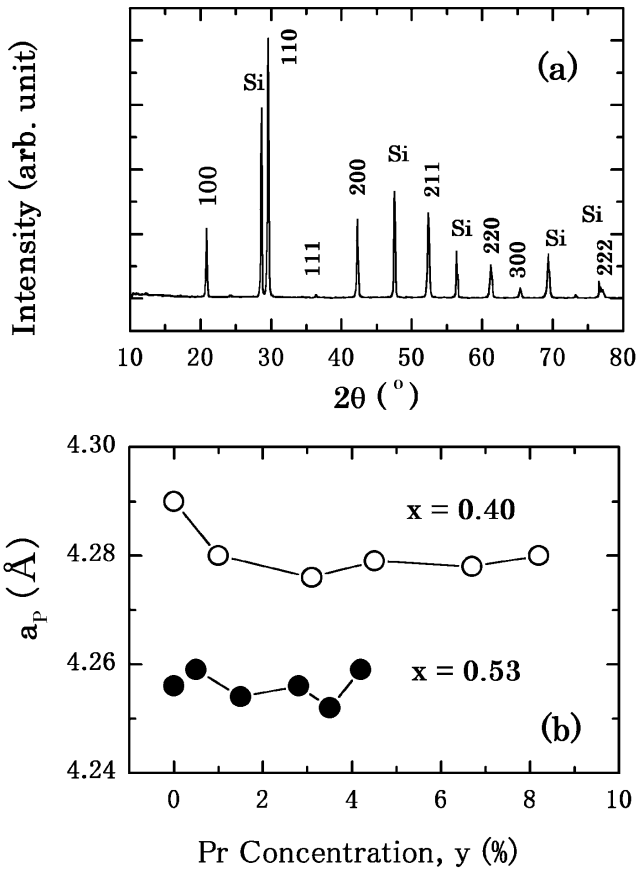

Figure 2. (a) The powder x-ray diffraction pattern of $Ba_{1-x}K_xBi_{1-y}Pr_yO_3$ with $x = 0.40$ and $y = 8.2\%$. (b) The lattice parameter, a_p of $Ba_{1-x}K_xBi_{1-y}Pr_yO_3$ plotted against Pr concentration.

T_c are decreasing with increasing Pr concentrations and not observed down to 2 K for the samples with $y = 8.2\%$ and 4.2% for $x = 0.40$ and 0.53, respectively. The inset in figure 3(a) for the sample with $x = 0.40$ and $y = 7.5\%$ shows T_c at 3.5 K.

In figure 4, T_c is plotted against Pr concentration y. For $x = 0.40$, as y increases, T_c decreases linearly at low y values but relaxes the rate once at ~5% and then falls at 8%. For $x = 0.53$, the rapid T_c suppression is observed only below $y = 1.5\%$ and a slow decrease is found up to $y = 4.1\%$. The T_c suppression rates, dT_c/dy near $y = 0$ are -3.2 ± 0.2 K/at.% and -3.1 ± 0.5 K/at.% for $x = 0.40$ and 0.53, respectively. They are close to each other. The transition width ΔT_c, which is defined as the difference of two temperatures where values of the susceptibility are at 10% and 90% from the minimal diamagnetic susceptibility, is as narrow as 2.5 K for samples with $x = 0.40$ and $y \leqslant 3.1\%$ and also for samples with $x = 0.53$ and $y \leqslant 2.1\%$, but, after decreasing the suppression rate, we find that ΔT_c increases for both series of samples. The Meissner fraction also decreases rapidly above $y = 3.1\%$ for $x = 0.40$ and above $y = 0.28$ for $x = 0.53$.

In order to analyse T_c behaviours for the Pr substitution, T_c data were fitted to the AG universal formula [1] for the rapid suppression region near $y = 0$:

$$\ln\left(\frac{T_c(y)}{T_c(0)}\right) = \Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2} + 0.14\frac{y}{y_{cr}}\frac{T_c(0)}{T_c(y)}\right) \tag{1}$$

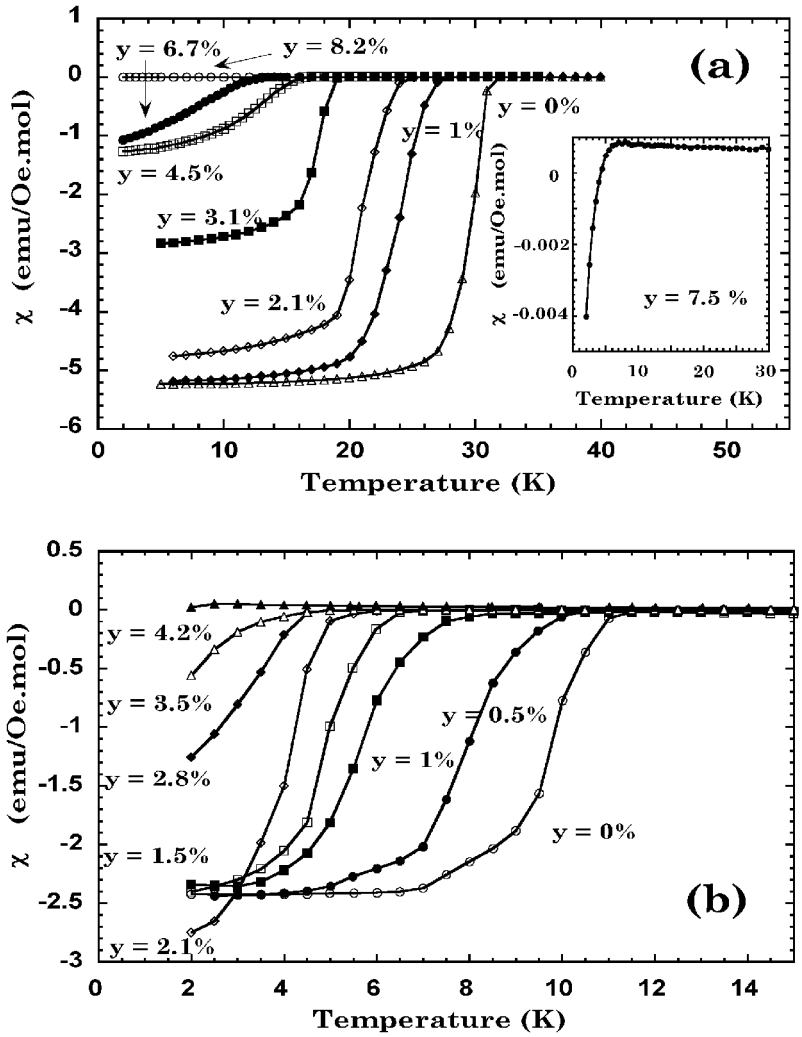

Figure 3. (a) Zero-field-cooled dc susceptibility against temperature of $Ba_{1-x}K_xBi_{1-y}Pr_yO_3$ with $x = 0.40$ at different y values. The inset is for $y = 7.5\%$. The applied magnetic field is 20 Oe for $y < 4.5\%$ and 5 Oe for the others. (b) Zero-field-cooled dc susceptibility for crystals with $x = 0.53$ under magnetic field of 5 Oe.

where Ψ is the digamma function and y_{cr} is the critical concentration where T_c would vanish. The AG theory is still valid in this system because the BKB has an s-wave order parameter and an electron as the charge carrier. As shown in figure 4, the T_c data coincide with the AG universal formula below the transition concentration, $y_{tr} = 3.5\%$ and 1.5% for $x = 0.40$ and 0.53, respectively and they deviate from the formula above those y_{tr} values lower than y_{cr}. The experimental critical concentration, y_{cr}.exp, where T_c completely vanishes, is larger than the critical concentration predicted by the AG theory, $y_{cr.AG}$. We plotted the normalized T_c data $(T_c(y)/T_c(0))$ against the normalized concentration $y/y_{cr.AG}$ in the inset of figure 4, which shows that T_c for the crystals with $x = 0.53$ survives in the higher normalized y than for the crystal with $x = 0.40$, though they start to deviate from the AG curves nearly at the same point.

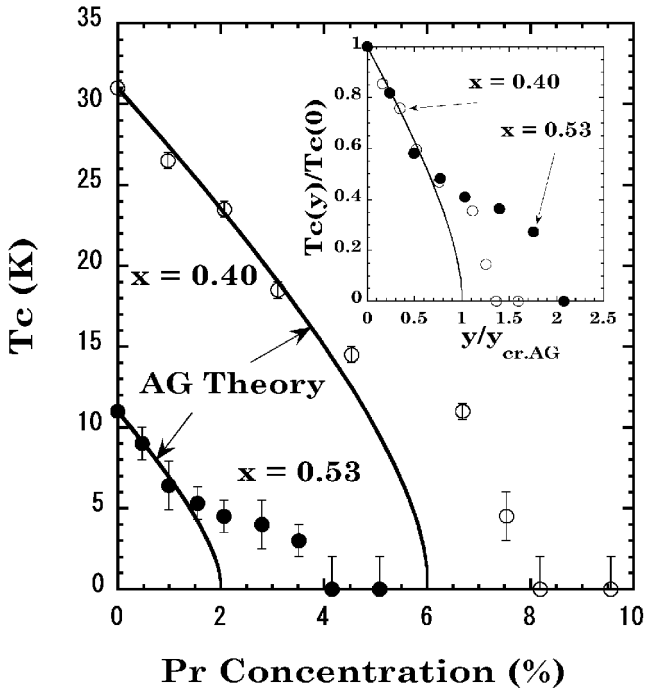

Figure 4. T_c against Pr concentration for single crystals of $Ba_{1-x}K_xBi_{1-y}Pr_yO_3$ with $x = 0.40$ and 0.53. The solid lines are the Abrikosov–Gor'kov (AG) formulae. The inset is the plot of the normalized T_c, $(T_c(y)/T_c(0))$ against the Pr concentration normalized to the AG critical concentration, $(y/y_{cr.AG})$.

We find that, in the lower concentration region of Pr, AG theory describes the T_c behaviour but, in the higher concentration region, T_c deviates from the theory. We note here that the rapid decrease of T_c near 0 K is still found, as if T_c obeyed the AG formula with different pair-breaking rates for $x = 0.40$ and 0.53.

The normal-state magnetic susceptibility, $\chi(y, T)$ for BKBP is found to exhibit a Curie–Weiss behaviour, though BKB exhibits only weak temperature dependent susceptibility in agreement with the previous result [22]. Figures 5(a) and (b) show plots of $1/[\chi(y, T) - \chi_0(y)]$ against temperature, where $\chi_0(y)$ is the temperature-independent contribution to the susceptibility obtained from the data at higher temperatures. The fitting to the Curie–Weiss equation,

$$\chi(y, T) = \chi_0(y) + \frac{C(y)}{T - \Theta(y)} \tag{2}$$

in which $C(y)$ is the Curie constant and $\Theta(y)$ is the Curie–Weiss temperature, was carried out in temperature range from 30 K to 250 K to avoid the influence of the superconducting fluctuation. The Pauli susceptibility including the diamagnetic Landau contribution was estimated from $\chi_0(y)$ by subtracting the core-diamagnetic susceptibility contribution and the temperature independent part (TIP) susceptibility of the Pr ion using values in $BaPrO_3$ [23].

The Pr effective moment, $\mu_{eff,Pr}$ estimated from $C(y)$ is shown in figure 6(a). $\mu_{eff,Pr}$ remain constant at $1.0 \pm 0.1\ \mu_B$ for $x = 0.40$ and $1.2 \pm 0.1\ \mu_B$ for $x = 0.53$, respectively. These values are close to the effective moments of Pr in the $BaPrO_3$ ($0.68\ \mu_B$) [23], but small compared with those of the Pr^{3+} ($3.58\ \mu_B$) and Pr^{4+} ($2.54\ \mu_B$) free-ion effective moments. The

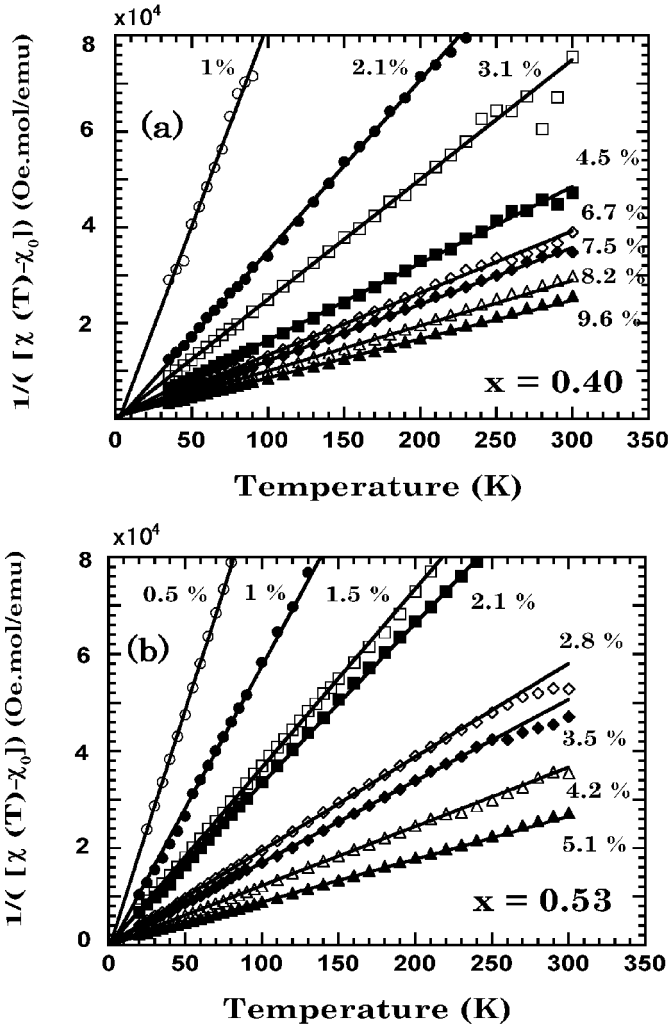

Figure 5. (a) Plot of $1/[\chi(y, T) - \chi_0(y)]$ against temperature for $Ba_{1-x}K_xBi_{1-y}Pr_yO_3$ with $x = 0.40$ and various y, in the temperature range from 35 to 300 K. (b) Plot of $1/[\chi(y, T) - \chi_0(y)]$ against temperature for $Ba_{1-x}K_xBi_{1-y}Pr_yO_3$ with $x = 0.53$ and various y, in the temperature range from 35 to 300 K.

small Pr effective moment could be understood from the following viewpoints: (1) the crystal field effect, which quenches the magnetic moment of the Pr ion, and (2) the effect of conduction electrons, which screen the crystalline field. The conduction-electron screening of the crystal field seems to lead to larger Pr effective moment in the metallic BKB system than in $BaPrO_3$.

The Curie–Weiss temperature Θ can be obtained from the abscissa intercept of the extrapolated data line in figure 5. Θ changes systematically with Pr concentration as shown in figure 6(b). The slope of the plot of $1/[\chi(y, T) - \chi_0(y)]$ against temperature shows a tendency that Θ becomes negative as Pr concentration increases. The Θ values, which are only a few Kelvin, are reasonable since Θ in $BaPrO_3$ is reported to be -25 K [24]. The positive Θ values below $y = 3.5\%$ and 1.5% for $x = 0.40$ and 0.53, respectively, indicate the ferromagnetic interaction between Pr moments in these regions. Above these y values, negative Θ mean

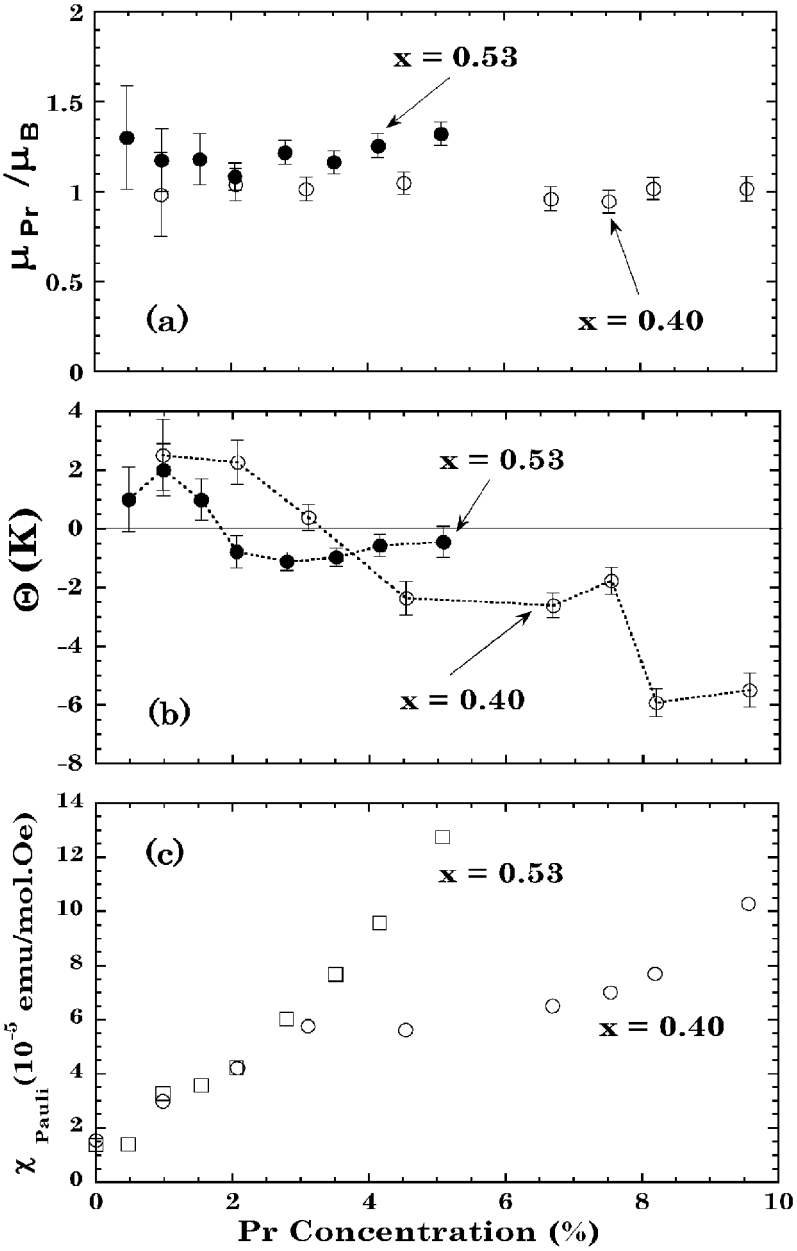

Figure 6. (a) The Pr effective moment plotted against Pr concentration, y for $Ba_{1-x}K_xBi_{1-y}Pr_yO_3$. (b) The Curie–Weiss temperature, Θ against Pr concentration. (c) The plot of Pauli susceptibility against Pr concentration.

anti-ferromagnetic interaction. We note that these y values coincide with y_{tr} at which T_c starts to deviate from the AG theory. A sudden drop of Θ at $y = 8\%$ for $x = 0.40$ can be attributed to the antiferromagnetic super-exchange interaction. Since the average distance between Pr ions at this concentration is nearly twice the lattice parameter (a_p), a considerable number of pairs of Pr ions can interact through oxygen ions.

The Pauli susceptibility $\chi_{Pauli}(y)$ is plotted against Pr concentration in figure 6(c). For samples with $x = 0.40$, $\chi_{Pauli}(y)$ changes linearly at first up to $y = 3\%$ and then super-linearly after exhibiting a plateau. The boundary concentration $y = 3\%$ nearly coincides with the transition y_{tr} from the ferromagnetic to anti-ferromagnetic interaction. Meanwhile, for the samples with $x = 0.53$, the non-linear dependence of $\chi_{Pauli}(y)$ can be found above $y_{tr} = 0.15\%$, but it is difficult to find the plateau and the linear region below y_{tr}, since the region with the ferromagnetic interaction is narrower than for $x = 0.40$.

4. Discussion

The sign change of the Curie–Weiss temperature Θ as shown in figure 6(b) can be understood through the RKKY interaction [25] between Pr ions through the conduction electrons. In the molecular field approximation in the RKKY interaction, Θ can be expressed as follows:

$$\Theta = (3\pi n^2 3/k_B E_F) G^2 (g_J - 1)^2 J(J+1) \sum_{ij} F(k_F R_{ij}) \, \mathrm{e}^{-R_{ij}/\lambda} \tag{3}$$

where k_F is the Fermi wave-number, E_F is the Fermi energy, G is the exchange integral of the Pr-ion moment with the conduction electron, $(g_J - 1)^2 J(J+1)$ is the de Gennes factor, R_{ij} is the distance between Pr ions, λ is the mean free path of the conduction electron, which is about the nearest R_{ij} at most, and

$$F(k_F R) = [\sin(2k_F R) - (2k_F R)\cos(2k_F R)]/(2k_F R)^4 \tag{4}$$

is the Ruderman–Kittel function, the R_{ij} summation of which determines the sign of Θ. Values of k_F can be estimated by using the conduction-electron density [26], $n = 1.25(1 - x) \times 10^{22}$ cm^{-3} in the free electron model. R_{ij} equals $a_P y^{1/3}$ on assuming the Pr ions residing in a simple cubic regular lattice, and Θ changes sign from positive to negative at the concentration $y \approx 5.1\%$ and 3.8%, respectively. These values are close to the observed values, $y_{tr} = 3.1\%$ and 1.5% for $x = 0.40$ and 0.53. Random distribution of the Pr ions would lead to smaller transition concentrations. For the smaller concentration, the coupling between Pr moments would disappear, since λ would be smaller than the nearest R_{ij}.

Now, let us discuss the suppression of T_c by Pr doping. The decreasing of T_c in the BKBP is dominantly caused by the magnetic impurity time-reversal pair-breaking effect described by the AG theory rather than the effect of carrier concentration variation. If we assume that the effect of Pr also reduces the free carrier concentration, the combination of this effect with the magnetic pair-breaking leads to stronger T_c suppression contrary to our observation of the relaxation of decreasing T_c. In the AG theory, the pair-breaking parameter which governs the suppression of T_c can be written as $\alpha = 2\pi N(0) G^2 (g_J - 1)^2 J(J+1)$, where $N(0)$ is the density of states of undoped BKB at Fermi level, G is the exchange integral between Pr and the conduction electron and $(g_J - 1)^2 J(J+1)$ is the de Gennes factor. The constant effective moment ($\mu_{eff}/\mu_B = g_J[J(J+1)]^{1/2}$) as shown in figure 6(a) indicates that the de Gennes factor is also constant. Therefore, we must search for another theory for the observed T_c suppression behaviour than AG theory. The crystal-field effect theory on T_c for the singlet ground state cannot be applied to our case, in which the Pr in the BKB is in the tetravalent state or in the Kramers state [3]. Supposing that the Pr were not in the tetravalent state, the crystal field effect must show a smooth and continuous drop of T_c near 0 K, contrary to the rapid decrease of T_c observed in BKBP.

The other possibility might be the Kondo effect. The Kondo system has a large initial superconducting suppression rate, for example $(La, Sm)Sn_3$ has an initial suppression of $(dT_c/dy)_{y=0} = -4.32$ K/at.% Sm [27], close to Pr-doped BKB. However, the Kondo

temperature in the BKB system is predicted to be small, in the order of 10^{-7} K with equation $T_K \approx T_F \exp(-1/|JN(0)|)$, with Fermi temperature, $T_F = 1210$ K, density of states, $N(0) = 0.46$ eV^{-1}/fu [22], and the s–f exchange interaction J within values of 0.01 and 0.1 eV fu, since BKB has a low density of states at the Fermi level. This value is extremely small compared with T_c; therefore T_c should follow the AG theory. In BKB except for the lowest temperature, the Kondo singlet state might not occur since the carrier density in this system is too low to effectively screen the localized f electron.

Since we have observed that the Curie–Weiss temperature changes sign from positive to negative at the concentration y_{tr}, the antiferromagnetic coupling for pairs of Pr moments seems to be the origin of the relaxed decreasing rate of T_c. In the lowest Pr concentration region adjacent to the antiferromagnetic coupling region, the mean free path of the conduction electron would be shorter than the distance between Pr ions. The pair-breaking effect is well described by a single impurity scattering or the AG theory. In a higher Pr concentration with a random distribution of Pr ions, the antiferromagnetical pairs of Pr moments are magnetically non-active, but a small number of isolated Pr moments could play a role for the pair breaking through spin fluctuation. Since the Curie–Weiss temperature Θ resides near T_c, the superconducting fluctuation inhibits observation of the susceptibility decrease due to the non-magnetic pairs of Pr moments near Θ. Bennemann [30] has calculated that the electronic scattering by the localized spin fluctuations decreased with the decreasing of temperature with the assumption that the coupling between magnetic impurities is antiferromagnetic. This also explains that T_c in the crystals with $x = 0.53$ survives more because it has T_c lower than in $x = 0.40$. The non-magnetic pairs also might increase ΔT_c and decrease the Meissner fraction as found in figure 3.

We have observed a remarkable increase of the Pauli susceptibility, which is linear in the low concentration region and super-linear in the antiferromagnetically coupled region of Pr moments as shown in figure 6(c). This indicates the increasing of the effective mass of the conduction electron in Pr-doped BKB, correlated with the presence of the 4f electron. This may remind us a heavy-electron system such as CeX, in which the Kondo lattice is known to form to increase the density of states of conduction electrons. In BKBP, however, we have discussed above that the forming of the Kondo state is not possible except for the lowest temperatures, and then the same mechanism as in the heavy electron system is not applicable in this system.

In $Rh_{1-x}Ni_x$ alloy, the susceptibility and the specific heat coefficient are known to increase with Ni content in the paramagnetic region due to the electron paramagnon interaction [28, 29]. In BKBP, spin polarizations or fluctuations are induced by the presence of Pr ions, and then the possible electron paramagnon interaction in addition to the electron–phonon interaction in the ferromagnetic or antiferromagnetic-coupled regions seems to enhance the electron mass parameter. The concentration dependence of the susceptibility in figure 6(c) is consistent with the picture, since the electron paramagnon interaction seems proportional to the content of the magnetic centres, which is linear and quadratic with the Pr concentration for the ferromagnetically and anti-ferromagnetically coupled regions, respectively. The electron paramagnon interaction is known to suppress T_c, since the interaction works as a repulsive one for the Cooper pair. Since the present data for T_c are consistent with the AG theory for the pair breaking in the lower concentration region, additional suppression for T_c by the electron–paramagnon interaction seems small.

5. Conclusion

We have experimentally investigated the superconducting critical temperature in Pr-doped BKB. T_c follows the AG formula at lower concentration, but deviates from the AG curve above a transition concentration y_{tr} with a lower suppression rate. From the normal-state magnetic

susceptibility, we have found that the magnetic interaction between Pr moments through RKKY interaction is ferromagnetic below y_{tr} and antiferromagnetic above y_{tr}. The electron scattering by the antiferromagnetically coupled Pr moment causes lower suppression rate of T_c. The Pauli susceptibility increases linearly and super-linearly for the ferromagnetically and antiferromagnetically coupled regions of Pr, respectively. We have proposed the mass enhancement effect by the electron paramagnon interaction for this anomalous behaviour.

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