Mixed valency of Pr in a $Y_{1-x}Pr_xBa_2Cu_3O_7$ bilayer

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A bilayer model of $Y_{1-x}Pr_xBa_2Cu_3O_7$ is presented, and the Brillouin-Wigner theory in the large-N limit is adopted to study the mixed-valence behavior of praseodymium. The chemical valence N_f (or N_{f0}) of the Pr dopant as functions of the energy-level difference E_f between $4f$ configurations, the mixing interaction strength v_k between $4f$ electrons and conduction holes, and the hole content P are investigated and discussed.

I. INTRODUCTION

$PrBa_2Cu_3O_7$ has attracted intensive attention for its unique property of being identical in structure to $YBa_2Cu_3O_7$ with insulating behavior,[1,2] and up to date the reason for this is still in suspense.[3–8] One of the most important causes is that the chemical valence N_f of the Pr dopant in the $Y_{1-x}Pr_xBa_2Cu_3O_7$ system remains uncertain; some researchers suggest N_f is 4 (Pr^{4+}),[3,4] and others insist on the valence 3 for the Pr ion (Pr^{3+}).[5,6]

Pr, as a rare-earth impurity, may have two different ionic configurations;[7–9] (i) $Pr^{4+}(4f^1)$ with energy level E_1 and angular momentum $J_1=\frac{5}{2}$, and (ii) $Pr^{3+}(4f^2)$ with energy level E_2 and angular momentum $J_2=4$. For an isolated ion of Pr, $E_2<E_1$, so that the $4f^2$ configuration is the ground state and Pr^{3+} shows its magnetic moment. In compound systems like $Y_{1-x}Pr_xBa_2Cu_3O_7$, however, the energy levels of the two configurations $4f^1$ and $4f^2$ are shifted as $E_1\rightarrow E_1+\tilde{E}_1$ and $E_2\rightarrow E_2+\tilde{E}_2$ owing to the mixing interaction between the Pr $4f$ electrons and the host conduction electrons (holes).[10–13] In this way, the valence of the doped Pr ion is neither 3 (Pr^{3+}) nor 4 (Pr^{4+}), and at the large-$N(N=2J+1)$ limit, according to the Brillouin-Wigner theory,[10–13] the two energy levels are probably reversed as $E_2+\tilde{E}_2>E_1+\tilde{E}_1$, and the average valence of the Pr impurity maybe lies between 3 and 4. In order to find an accurate solution to these problems, therefore, it is necessary to investigate the mixed-valence behavior of Pr in the $Y_{1-x}Pr_xBa_2Cu_3O_7$ system. As a beginning, in this paper, we consider a $Y_{1-x}Pr_xBa_2Cu_3O_7$ bilayer, the unit cell of the system. We propose a bilayer model and then adopt the Brillouin-Wigner theory to study its mixed-valence fluctuation.

II. MODEL AND THEORY

A. Model

The $Y_{1-x}Pr_xBa_2Cu_3O_7$ bilayer model, in this paper, consists of two CuO_2 planes with Y ions, some of which are substituted with Pr dopants, between them. The two CuO_2 planes are coupled by holes (electrons) hopping from one plane to another, and also by the mixing interaction between holes and Pr impurities, thus leading to valence fluctuation.

The model Hamiltonian to describe the bilayer can be written as

$$\begin{aligned} H&=H_0+H' ,\\ H_0-\mu N&=\sum_{m_1}(E_1-\mu)X_{m_1m_1}+\sum_{m_2}(E_2-\mu)X_{m_2m_2}\\ &\quad+\sum_{l}\sum_{k\sigma}(\xi_k-\mu)a^{\dagger}_{lk\sigma}a_{lk\sigma}+t_z\sum_{k\sigma}a^{\dagger}_{1k\sigma}a_{2k\sigma} ,\\ H'&=\sum_{l}\sum_{k\sigma}\sum_{m_1m_2}(v_k a^{\dagger}_{lk\sigma}X_{m_2m_1}+\text{H.c.}) . \end{aligned} \tag{1}$$

In this case l ($l=1,2$) labels the location of the CuO_2 plane, t_z is the inter-CuO_2-plane hopping constant of holes, and $a^{\dagger}_{lk\sigma}$ and $a_{lk\sigma}$ represent creation and annihilation operators of conduction holes in the CuO_2 plane, respectively; $X_{m_1m_2}=|m_1\rangle\langle m_2|$ represents the Hubbard's projection operator with $|m_1\rangle,|m_2\rangle$ denoting $4f^1,4f^2$ configurations,[17] and N_1 and N_2 are the degeneracies of $4f$ configurations (where $N_1=2J_1+1$, $N_2=2J_2+1$), respectively; μ is the Fermi level, v_k stands for the mixing interaction strength between holes of the extended states and $4f$ electrons, and ξ_k, the energy spectrum of the conduction hole inside the CuO_2 plane, can be expressed in the tight-binding form as

$$\xi_k=4t-2t[\cos(k_xa)+\cos(k_ya)] , \tag{2}$$

where a is the intraplane lattice constant of the $Y_{1-x}Pr_xBa_2Cu_3O_7$ bilayer.

B. Partition function and energy shifts

By extending the hybridization term H' which is now taken as a perturbation, we can express the partition function of the system as[14,15]

$$Z/Z_0-1=\sum_{n=1}^{\infty}(-1)^n\int d\tau_1 d\tau_2\cdots d\tau_n \times\langle H'(\tau_1)H'(\tau_2)\cdots H'(\tau_n)\rangle_0 , \quad (3)$$

where Z_0 represents the partition function of the pure $YBa_2Cu_3O_7$ bilayer system. In this way, the second-order partition function of the system is[14,15]

$$Z^{(2)}/Z_0=(-1)^2\int_0^{\beta}d\tau_1\int_0^{\tau_1}d\tau_2\langle H'(\tau_1)H'(\tau_2)\rangle_0$$
$$=\int_0^{\beta}d\tau_1\int_0^{\tau_1}d\tau_2\left\langle\sum_l\sum_{k\sigma}\sum_{m_1m_2}\sum_{l'}\sum_{k'\sigma'}\sum_{m_1'm_2'}[v_k a_{lk\sigma}^{\dagger}X_{m_2m_1}+\text{H.c.}](\tau_1)[v_{k'}a_{l'k'\sigma'}^{\dagger}X_{m_2'm_1'}+\text{H.c.}](\tau_2)\right\rangle_0 . \quad (4)$$

Wick's theorem can be applied only to products of operators of conduction holes,[16] the thermodynamic expectation of the products of $4f$ projection operators can be determined directly with the help of the properties of these operators,[17] and the time-ordered integral can be transformed into a contour integral.[18] Consequently, the second-order partition function as shown above is changed into[10–13]

$$Z^{(2)}/Z_0=\oint_C\frac{dZ}{2\pi i}\frac{e^{-\beta Z}}{Z^2}\sum_{k\sigma}\sum_{m_1m_2}v_k^2\left[\tilde{P}_{m_1}\frac{2f(t_z-\xi_k)}{Z-E_f-\xi_k+t_z}+\tilde{P}_{m_2}\frac{2f(t_z+\xi_k)}{Z+E_f+\xi_k+t_z}\right] , \quad (5)$$

where

$$\tilde{P}_{m_1}=\frac{1}{N_1+N_2e^{-\beta(E_f+\tilde{E}_f)}} ,$$
$$\tilde{P}_{m_2}=\frac{e^{-\beta(E_f+\tilde{E}_f)}}{N_1+N_2e^{-\beta(E_f+\tilde{E}_f)}}$$

are the occupation probabilities of the shifted $4f^1$ and $4f^2$ configurations, respectively, and $E_f=E_2-E_1$ is the energy difference between the $4f^1$ and $4f^2$ configurations. $\tilde{E}_f=\tilde{E}_2-\tilde{E}_1$ is the shift of E_f with $\tilde{E}_1$ and $\tilde{E}_2$ being the shifts of E_1 and E_2 due to the mixing interaction between $4f$ electron and conduction hole. $f(x)$ is the Fermi distribution function. For the large-N limit, in terms of the Brillouin-Wigner theory,[10–13] we can describe $\tilde{E}_1$ and $\tilde{E}_2$ in the self-consistent forms

$$\tilde{E}_1=\sum_{k\sigma}\sum_{m_2}v_k^2\frac{2f(t_z-\xi_k)}{\tilde{E}_1-E_f-\xi_k+t_z} , \quad (6a)$$

$$\tilde{E}_2=\sum_{k\sigma}\sum_{m_1}v_k^2\frac{2f(t_z+\xi_k)}{\tilde{E}_2+E_f+\xi_k+t_z} . \quad (6b)$$

Due to the existence of the factor $f(t_z+\xi_k)$, the shift $\tilde{E}_2$ may be much smaller, i.e., the energy level E_2 of the $4f^2$ configuration is hardly altered even in the compound bilayer; therefore the mixed-valence behavior of Pr is mainly attributed to the energy shift $\tilde{E}_1$ of the $4f^1$ configuration. When $t_z\to 0$, there will be no direct interplane coupling and the result somewhat resembles that of the $Th_{1-x}Ce_x$ system.[10–13]

C. Mixed-valence N_{f0}

As in the normal state, the mixed-valence N_{f0} of the rare-earth impurity ion can be defined as the occupation probability of the $4f^2$ configuration,[10–12]

$$N_{f0}=\sum_{m_2}\langle X_{m_2m_2}\rangle=\tilde{P}_1\frac{\partial\tilde{E}_1}{\partial E_f}+\tilde{P}_2\left[1+\frac{\partial\tilde{E}_2}{\partial E_f}\right] , \quad (7)$$

where

$$\tilde{P}_1=\sum_{m_1}\tilde{P}_{m_1} ,$$
$$\tilde{P}_2=\sum_{m_2}\tilde{P}_{m_2}$$

are the total occupancies of the shifted $4f$ configurations. By solving simultaneously Eqs. (6) and (7), the numerical results for N_{f0} as functions of E_f, v_k, and hole content P are obtained and shown in Figs. 1, 2, and 3, respectively, with $t=0.5$ eV and $t_z=0.1$ eV.

As we know, the chemical valence N_f of the rare-earth

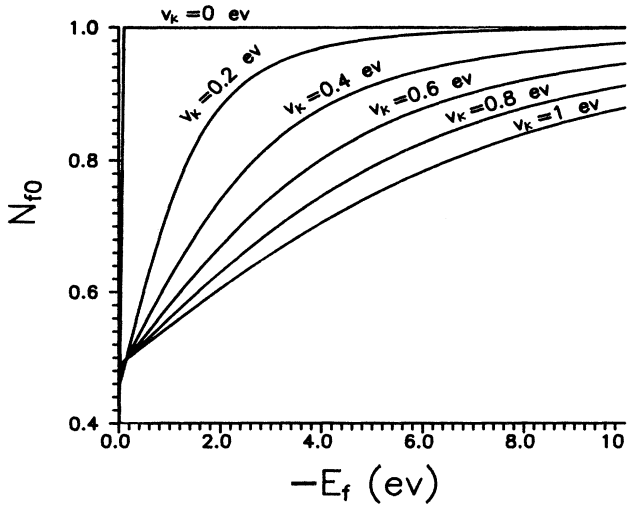

FIG. 1. Mixed-valence N_{f0} as a function of the energy-level difference E_f between the $4f$ configurations (where $P=0.15$).

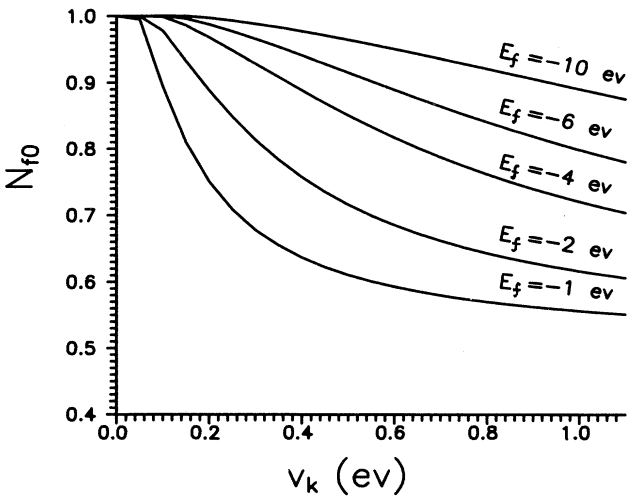

FIG. 2. Mixed-valence N_{f0} as a function of the mixing interaction strength v_k between the $4f$ electrons and holes of the extended state in the CuO_2 plane (where $P=0.1$).

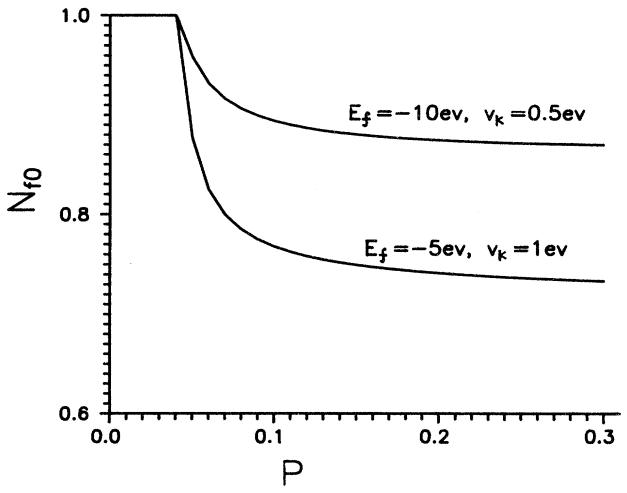

FIG. 3. Mixed-valence N_{f0} versus the hole content P with different parameters v_k and E_f.

ion indicates the number of ionized electrons of the ion, and in this case the chemical valence of the Pr impurity is[10–13]

$$N_f=3+(1-N_{f0})\ . \tag{8}$$

Figures 1 and 2 show that in the $Y_{1-x}Pr_xBa_2Cu_3O_7$ bilayer, owing to the mixing interaction between the $4f$ electron and conduction hole, the chemical valence N_f of the Pr ion is neither 3 (Pr^{3+}) nor 4 (Pr^{4+}), but a fractional value between them. N_{f0} decreases as v_k increases or as the absolute value $|E_f|$ decreases. It is not difficult for us to understand that the stronger is the mixing interaction strength and the smaller is the difference of energy levels between $4f^1$ and $4f^2$ configurations, the easier is the reversal of the $4f$ energy levels, thus leading to greater occupancies of the $4f^1$ configuration. If $v_k=0$, there is no influence of the Pr impurity on the conduction holes in the CuO_2 plane or of the conduction holes on Pr; therefore the Pr ion will remain as Pr^{3+}.

Figure 3 shows that, if the hole content P is less than 0.04, there is no mixed-valence behavior and the chemical valence of Pr will remain 3 (Pr^{3+}), and that when P surpasses 0.08 little influence of hole content P over N_f is observed. The result reveals that in the normal state there is a threshold value of hole content below which the mixed-valence fluctuation does not occur.

III. CONCLUSION

We presented a $Y_{1-x}Pr_xBa_2Cu_3O_7$ bilayer model, and applied the $1/N$ expansion of the Brillouin-Wigner theory to the mixed-valent behavior of the dopant Pr ion in the bilayer. The relationships of chemical valence N_f (or mixed-valence N_{f0}) versus E_f, v_k, and P were investigated.

The results provide a clearly physical picture of the peculiar nature of the $Y_{1-x}Pr_xBa_2Cu_3O_7$ system, based on which further work on the superconductivity of the bilayer has also been completed in another paper.[19]

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