Theoretical model for the low-temperature ordering of Pr in $PrBa_2Cu_3O_{6+x}$

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Theoretical model is presented to describe the anomalous ordered phase of Pr ions in $PrBa_2Cu_3O_{6+x}$ below $T_{Pr} \approx 12-17$ K. The model considers the Pr multipole degrees of freedom and coupling between the Cu and Pr subsystems. We identify the symmetry allowed coupling of Cu and Pr ions and conclude that only an *ab*-plane Pr dipole ordering can explain the Cu spin rotation observed at T_{Pr} by neutron diffraction by Boothroyd *et al.* [Phys. Rev. Lett. **78**, 130 (1997)]. A substantial enhancement of the Pr ordering temperature is shown to arise from the Cu-Pr coupling which is the key for the anomalous magnetic behavior in $PrBa_2Cu_3O_{6+x}$.

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I. INTRODUCTION

Nonsuperconducting $PrBa_2Cu_3O_{6+x}$ compound attracted considerable attention in the last two decades because of its intriguing magnetic and electronic properties within the $ReBa_2Cu_3O_{6+x}$ family of compounds (Re=rare-earth atom).[1] In spite of the great efforts from both experimental and theoretical sides, numerous problems remain unresolved such as the suppression of superconductivity and the nature of the long-range ordered state of Pr sublattice with a unique, about an order of magnitude larger than for other rare-earth atoms, ordering temperature. Although, there exists a discussion whether the ground state of $PrBa_2Cu_3O_{6+x}$ is really a nonsuperconducting, insulating material with a magnetically ordered Cu and Pr sublattices, herein we consider this modification of $PrBa_2Cu_3O_{6+x}$ as "canonical" and treat it solely herein. We note that superconductivity in $PrBa_2Cu_3O_{6+x}$ was reported[2] and a nonmagnetic Pr ground state was found by ^{141}Pr NMR.[3] It was suggested that these observations may result from a nonstoichiometric compound, i.e., when Pr occupies only about a half of the rare-earth sites, and the other half is occupied by the nonmagnetic Ba.[4]

The theoretical model of Fehrenbacher and Rice, i.e., the hybridization of Pr $4f$ and the nearest-neighbor O $2p$ orbitals is the most accepted model to account for the absence of superconductivity in $PrBa_2Cu_3O_{6+x}$. It is suggested that the localization of holes in the hybridized $4f$-$2p$ orbitals renders the material nonsuperconducting.[5] Although the nonsuperconducting nature of $PrBa_2Cu_3O_7$ compound is a challenging and interesting problem, we concentrate herein exclusively on the low-temperature Pr ordering.

$PrBa_2Cu_3O_{6+x}$ is an insulator for every x and the Cu spins in the CuO_2 planes order antiferromagnetically (AFM) at temperatures of $T_N \sim 350$ K and 250 K for $x=0$ and $x=1$, respectively.[6–8] As the temperature is further decreased, the Pr sublattice also undergoes a phase transition[9,10] in the temperature range $T_{Pr} \sim 12-17$ K depending on x, which appears as an anomaly in the temperature dependence of thermodynamic quantities.[11,12] Mössbauer spectroscopy,[13] neutron diffraction,[8,11,12] and NMR (Refs. 3 and 14) showed that the Pr magnetic moments order antiferromagnetically below T_{Pr}. However, there is no consensus among these experiments with respect to the magnitude of the ordered Pr moment, its direction, and the nature of this transition.

Neutron-diffraction studies found 0.56 μ_B ($x=0.92$) and 1.15 μ_B ($x=0.35$) ordered moment with direction tilted out from the *ab* plane.[8] The rotation of Cu moments within the CuO_2 plane was found to accompany the Pr ordering,[8,15] which was suggested to result from the strong coupling between the Pr and Cu subsystems. However, the magnitude of the coupling, its character, and its influence on the magnitude of the ordered Pr magnetic moment, and for the ordering temperature is yet unexplained.

We give herein a comprehensive description of the Pr ordering in $PrBa_2Cu_3O_6$ on the basis of a model of localized $4f^2$ electrons of the Pr ion. We construct the general form of the Cu-Pr interaction allowed by the symmetry and identify the Pr order parameter from the rotation of Cu spins below T_{Pr} observed by neutron diffraction.[8,15] Although pseudodipole Cu-Pr interaction has been already proposed,[8,15,16] we derive the Cu-Pr interaction in general including all Pr multipole moments and arbitrary wave vectors. We describe a crystalline electric field (CEF) model which takes a ground-state quasitriplet composed by a doublet and a singlet states and also includes coupling between the Pr and Cu subsystems. This low-energy scheme is consistent with the neutron-diffraction results[11] and also with the high-temperature susceptibility data.[17] We also discuss the enhancement of the Pr ordering temperature due to the Cu-Pr coupling and the magnitude of Pr magnetic moment in the ordered state.

II. GENERAL FORM OF THE Cu-Pr INTERACTION

In $PrBa_2Cu_3O_6$, the Cu spins are antiferromagnetically ordered along the [100] direction in the CuO_2 planes with the ordering vector $\mathbf{Q}=[\pi/a, \pi/a, \pi/c]$ below the temperature $T_{Cu} \approx 350$ K (phase AFI).[8] As the temperature is further decreased, the Pr sublattice also undergoes an ordering at temperature $T_{Pr}=12$ K. This ordering is accompanied by the rotation of Cu spins within the CuO_2 planes in such a way that the new spin structure is noncollinear along the c direction (phase AFIII).[8,15,18] The Cu spin rotation is characterized by the ordering vector $\tilde{\mathbf{Q}}=[\pi/a, \pi/a, 0]$. The Cu spin structure

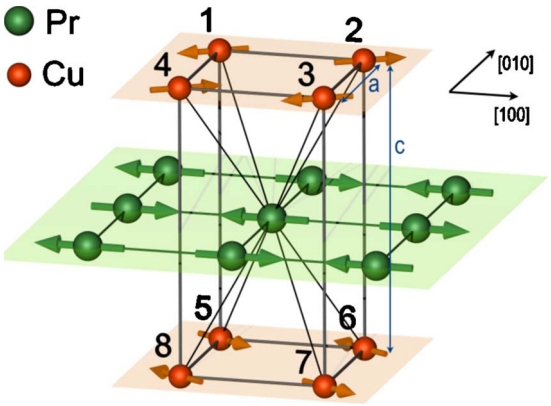

FIG. 1. (Color online) Magnetic structure of Cu spins in the CuO_2 planes and Pr dipole moments in the *ab* plane in the temperature range $T \leq T_{Pr}$. The central Pr ion in the *ab* plane is located at position $\mathbf{r}_0=(0,0,0)$ and the numbers label the Cu sites, i.e., Cu[1–8] used in the text.

in the CuO_2 planes is shown in Fig. 1 in the temperature range $T \leq T_{Pr}$.

First, we construct the invariant form of the interaction between the multipole moments of a Pr ion at position $\mathbf{r}_0=(0,0,0)$ and the surrounding eight Cu spins, Cu[1–8], shown in Fig. 1. Although the local symmetry at Pr site is tetragonal, a Cu-Pr pair has lower symmetry. For example, the Cu[1]-Pr pair has reflection symmetry with respect to the [1,1,0] mirror plane. The transformation of total angular momentum $\mathbf{J}$ of Pr ion under this operation is: $J_x \rightarrow J_y$, $J_y \rightarrow J_x$, and $J_z \rightarrow -J_z$. The same transformation is applied for the Cu spin $\mathbf{S}$. Thus, spin operators $J_x - J_y (S_x - S_y)$ and $J_z (S_z)$ are odd while $J_x + J_y (S_x + S_y)$ is even under this reflection. Not only the bilinear products of the Pr dipole moments and Cu spins appear in the interaction but also the bilinear products of rank-3 octupole and rank-5 triakontadipole[19] operators of Pr ion and Cu spins since they are allowed by the time-reversal symmetry. The octupole operators T_z^β and $T_x^\beta - T_y^\beta$ are even while T_{xyz} and $T_x^\beta + T_y^\beta$ are odd operators under the present transformation. In the case of tetragonal symmetry, there is one more independent magnetic operator, namely, the rank-5 triakontadipole operator $V_{1u}=J_x J_y J_z (J_x^2 - J_y^2)$ which is even under the present reflection. Thus, the invariant form of the interaction for the Cu[1]-Pr pair is constructed as

$$\begin{aligned}\mathcal{H}_{\mathrm{I}}^{\mathrm{Cu\text{-}Pr}}[1] = {} & (S_x + S_y)[c_{11}(J_x + J_y) + c_{12} T_z^\beta + c_{13} A_{1u}] \\ & + (S_x - S_y)[c_{21}(J_x - J_y) + c_{22} J_z + c_{23} T_{xyz}] \\ & + S_z[c_{31}(J_x - J_y) + c_{32} J_z + c_{33} T_{xyz}], \end{aligned} \tag{1}$$

where c_{ij} are constants which are not determined by the symmetry itself. The pair Cu[2]-Pr is connected to the pair Cu[1]-Pr by a $\pi/2$ rotation around the *c* axis. Under this operation the transformation of the angular-momentum components is given by $J_x \rightarrow -J_y$, $J_y \rightarrow J_x$, and $J_z \rightarrow J_z$. The same transformation holds also for the Cu spin components. Thus, the form of the interaction for the Cu[2]-Pr pair can be obtained from Eq. (1) by applying the $\pi/2$ rotation. Repeating further the appropriate rotations and reflections, the interaction can be obtained for all the eight Cu-Pr pairs. The Cu spin at position $\mathbf{r}$ is expressed by Fourier transformation as $\mathbf{S}(\mathbf{r})=\Sigma_{\mathbf{q}} \mathbf{S}^{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}}$. Using this expression, we obtain the total interaction as

$$\begin{aligned}\mathcal{H}_{\mathrm{I}}^{\mathrm{Cu\text{-}Pr}} = {} & \sum_{k=1}^{8} \mathcal{H}_{\mathrm{I}}^{\mathrm{Cu\text{-}Pr}}[k] \\ = {} & 8 \sum_{\mathbf{q}} \{(c_{11} + c_{21})(S_x^{\mathbf{q}} J_x + S_y^{\mathbf{q}} J_y) c_x c_y c_z \\ & + (c_{11} - c_{21})(S_x^{\mathbf{q}} J_y + S_y^{\mathbf{q}} J_x) s_x s_y c_z \\ & + c_{22} J_z [S_x^{\mathbf{q}} s_x c_y s_z - S_y^{\mathbf{q}} c_x s_y s_z] \\ & + c_{31} [J_x S_z^{\mathbf{q}} s_x s_y c_z - J_y S_z^{\mathbf{q}} c_x s_y s_z] + c_{32} J_z S_z^{\mathbf{q}} c_x c_y c_z \\ & + c_{12} T_z^\beta [S_x^{\mathbf{q}} s_x c_y s_z + S_y^{\mathbf{q}} c_x s_y s_z] \\ & + c_{13} A_{1u} [S_x^{\mathbf{q}} c_x s_y s_z + S_y^{\mathbf{q}} s_x c_y s_z] \\ & + c_{23} T_{xyz} [S_x^{\mathbf{q}} c_x s_y s_z - S_y^{\mathbf{q}} s_x c_y s_z] + c_{33} T_{xyz} S_z^{\mathbf{q}} s_x s_y c_z \}, \end{aligned} \tag{2}$$

where $c_k (s_k)$ denotes $\cos(q_k a/2)[\sin(q_k a/2)]$ for $k=x$, y, and $\cos(q_k c/2)[\sin(q_k c/2)]$ for $k=z$.

Now we discuss the multipole order of Pr sublattice based on expression (2). In phase AFI, the Cu spin component $S_x^{\mathbf{q}}$ with $\mathbf{q}=\mathbf{Q}$ is nonzero. In this phase there is no coupling between the Cu spins and Pr magnetic moments because the wave vector $\mathbf{Q}$ leads to $c_x=c_y=c_z=0$ and $s_x=s_y=s_z=1$, which gives that none of the terms survives in expression (2). On the other hand, a coupling of Cu spins and Pr moments is present in phase AFIII. The noncollinear Cu spin structure in phase AFIII can be described by the appearance of the extra spin component $S_y^{\tilde{\mathbf{Q}}}$ in addition to the component $S_x^{\mathbf{Q}}$. The wave vector $\tilde{\mathbf{Q}}$ gives $c_x=c_y=0$, $c_z=1$ and $s_x=s_y=1$, $s_z=0$ in expression (2). Together with the condition $S_y^{\tilde{\mathbf{Q}}} \neq 0$, we find that the only surviving term in the form of Cu-Pr interaction is the coupling $S_y^{\tilde{\mathbf{Q}}} J_x$. We note that the coupling $S_x^{\tilde{\mathbf{Q}}} J_y$ is also allowed by symmetry since the [100] and [010] domains in phase AFI are equivalent, which gives that the domains $\langle S_y^{\tilde{\mathbf{Q}}} \rangle \neq 0, \langle S_x^{\tilde{\mathbf{Q}}} \rangle = 0$ and $\langle S_x^{\tilde{\mathbf{Q}}} \rangle \neq 0, \langle S_y^{\tilde{\mathbf{Q}}} \rangle = 0$ are also equivalent.

Thus, we conclude that the neutron-diffraction result for the Cu spin rotation below T_{Pr} is compatible with Pr dipole moments lying along the crystalline [100] or [010] direction and no deviation from this direction is allowed by symmetry in contrast to the structure proposed in Ref. 8. Since the $S_y^{\tilde{\mathbf{Q}}} (S_x^{\tilde{\mathbf{Q}}})$ Cu spin components alternate along the *a* and *b* directions, the Pr dipole moments also form an AFM structure in the *ab* planes with the ordering vector $\tilde{\mathbf{Q}}$. The magnetic structure for the Cu spins and Pr dipole moments below T_{Pr} has the structure shown in Fig. 1.[20]

III. CEF MODEL FOR THE COUPLED Cu-Pr SYSTEM

We now turn to discuss a CEF model of the Pr ion $4f$ electrons to describe the Pr ordering in $PrBa_2Cu_3O_6$. The model consists of the coupled Pr and Cu subsystems and allows to calculate experimentally relevant quantities. The Pr ion has $4f^2$ electronic configuration in $PrBa_2Cu_3O_6$, which

gives $J=4$ as the total angular momentum based on the Hund's rule for the ground state. In the Pr subsystem, we consider AFM interaction between the in-plane J_x and J_y dipole moments described by the Hamiltonian

$$\mathcal{H}_{\mathrm{Pr}} = \frac{1}{2z}\sum_{\langle i,j\rangle} \Lambda[J_{x,i}J_{x,j} + J_{y,i}J_{y,j}], \tag{3}$$

where $z=4$ is the number of nearest-neighbor Pr ions and Λ is the coupling constant. Hamiltonian (3) is taken in a quasitriplet subspace, where the ground state is the doublet

$$|d_{\pm}\rangle = a|\pm 3\rangle + \sqrt{1-a^2}|\mp 1\rangle \tag{4}$$

with a near singlet excited state

$$|s\rangle = \frac{1}{\sqrt{2}}(|2\rangle + |-2\rangle), \tag{5}$$

where the states are expressed by the eigenstates of $\mathbf{J}$. The doublet and singlet states are separated by the gap Δ.[11,17] The other CEF levels lie at much higher energy therefore these can be neglected when describing the low-temperature behavior.

We treat the Cu subsystem phenomenologically and consider the free-energy expansion

$$\begin{aligned}\mathcal{F}_{\mathrm{Cu}} &= -\frac{1}{\beta}\ln \mathrm{Tr}_S(e^{-\beta\mathcal{H}_{\mathrm{Cu}}}) \\ &= a_s(\langle S_x^{\tilde{\mathbf{Q}}}\rangle^2 + \langle S_y^{\tilde{\mathbf{Q}}}\rangle^2) + b_s(\langle S_x^{\tilde{\mathbf{Q}}}\rangle^2 + \langle S_y^{\tilde{\mathbf{Q}}}\rangle^2)^2 \\ &\quad + 4c_s\langle S_x^{\tilde{\mathbf{Q}}}\rangle^2\langle S_y^{\tilde{\mathbf{Q}}}\rangle^2 + \mathcal{F}_{\mathrm{Cu}}^0,\end{aligned} \tag{6}$$

where $\mathcal{F}_{\mathrm{Cu}}^0$ contains the part corresponding to the Cu spin components, $S_x^{\mathbf{Q}}$ and $S_y^{\mathbf{Q}}$, which are not relevant for our discussion. We assume that $\langle S_{y(x)}^{\tilde{\mathbf{Q}}}\rangle$ is not critical around $T=T_{\mathrm{Pr}}$, thus, $a_s>0$. Parameters b_s and c_s determine the anisotropy as we discuss below.

The local coupling between the Cu and Pr subsystems is assumed as

$$\mathcal{H}_{\mathrm{c}} = z'\sum_i \lambda[J_{x,i}\langle S_y^{\tilde{\mathbf{Q}}}\rangle + J_{y,i}\langle S_x^{\tilde{\mathbf{Q}}}\rangle], \tag{7}$$

which corresponds to the only nonvanishing term in expression (2) for $\tilde{\mathbf{Q}}=[\pi/a,\pi/a,0]$. Here, $z'=8$ is the number of Pr nearest-neighbor Cu ions and λ is the Cu-Pr coupling constant. The series expansion of the total free energy has the form

$$\mathcal{F} = -\frac{1}{\beta}\ln \mathrm{Tr}_S(e^{-\beta\mathcal{H}_{\mathrm{Cu}}}) - \frac{1}{\beta}\ln \mathrm{Tr}_J(e^{-\beta(\mathcal{H}_{\mathrm{Pr}}+\mathcal{H}_{\mathrm{c}})}) \equiv \mathcal{F}_0 + \mathcal{F}_{\mathrm{Cu}}^0, \tag{8}$$

where

$$\begin{aligned}\mathcal{F}_0 &= a_J(\langle J_x^{\mathrm{Pr}}\rangle^2 + \langle J_y^{\mathrm{Pr}}\rangle^2) + b_J(\langle J_x^{\mathrm{Pr}}\rangle^2 + \langle J_y^{\mathrm{Pr}}\rangle^2)^2 + \lambda z'(\langle J_x^{\mathrm{Pr}}\rangle\langle S_y^{\tilde{\mathbf{Q}}}\rangle \\ &\quad + \langle J_y^{\mathrm{Pr}}\rangle\langle S_x^{\tilde{\mathbf{Q}}}\rangle) + a_s(\langle S_x^{\tilde{\mathbf{Q}}}\rangle^2 + \langle S_y^{\tilde{\mathbf{Q}}}\rangle^2) + b_s(\langle S_x^{\tilde{\mathbf{Q}}}\rangle^2 + \langle S_y^{\tilde{\mathbf{Q}}}\rangle^2)^2 \\ &\quad + 4c_s\langle S_x^{\tilde{\mathbf{Q}}}\rangle^2\langle S_y^{\tilde{\mathbf{Q}}}\rangle^2.\end{aligned} \tag{9}$$

The coefficient a_J is expressed in Eq. (9) as

$$a_J = \frac{1}{2}\Lambda^2\left(\frac{1}{\Lambda} + \frac{1}{\Delta}\frac{(2\gamma)^2(e^{-\Delta/T}-1)}{(e^{-\Delta/T}+2)}\right), \tag{10}$$

where $\gamma=1/4(9-2a^2+6\sqrt{7}a\sqrt{1-a^2})$ is the matrix element of the dipole operator, J_x, between the doublet and singlet states.

The quasitriplet subspace does not carry anisotropy with respect to the dipole moment components J_x and J_y, thus the Pr magnetic moment is isotropic in the ab plane for the Pr subsystem. However, there is a weak anisotropy even for the structurally tetragonal $x=0$ compound which gives rise to a degenerate [100] and [010] easy-axis ordering of the Cu spins in the AFI phase.[21] We introduce this anisotropy of the Cu sublattice through the parameters b_s and c_s in expression (6), which produces anisotropy also for the in-plane Pr magnetic moments through the Cu-Pr coupling. In the AFIII phase, these easy axes are inherited and the Cu spin ordering with wave vector $\tilde{\mathbf{Q}}$ is reproduced when $c_s>0$. We assume an infinitesimally small magnetic field along the [010] direction on the Cu sublattice, which resolves the [100], [010] degeneracy and stabilizes the solution $\langle J_x\rangle\neq 0$, $\langle J_y\rangle=0$ against the solution $\langle J_x\rangle=0$, $\langle J_y\rangle\neq 0$. The resulting Pr dipole moments have also a [100] easy axis.

In our scenario, the Pr dipole moments order at $T=T_{\mathrm{Pr}}$, and the order $\langle J_x\rangle\neq 0$ induces the $\langle S_y^{\tilde{\mathbf{Q}}}\rangle$ Cu spin component. From the condition $\partial\mathcal{F}/\partial\langle S_y^{\tilde{\mathbf{Q}}}\rangle=0$ we obtain

$$\langle S_y^{\tilde{\mathbf{Q}}}\rangle = -\frac{\lambda z'}{2a_s}\langle J_x^{\mathrm{Pr}}\rangle. \tag{11}$$

Substituting this expression into the free-energy expansion $\mathcal{F}$, the second-order coefficient of $\langle J_x^{\mathrm{Pr}}\rangle$ is obtained as

$$\tilde{a}_J \equiv a_J - \frac{(\lambda z')^2}{4a_s}. \tag{12}$$

We define the temperature T_0 which corresponds to the noncoupled system with $\lambda=0$ and the temperature T_{Pr} for the coupled system $\lambda\neq 0$. T_0 is obtained from the condition $a_J=0$, where the second-order coefficient has the form $a_J\equiv a_J'(T-T_0)$ in the vicinity of the phase transition. However, this transition temperature is modified due to the coupling to the Cu subsystem ($\lambda\neq 0$). T_{Pr} is obtained from the condition $\tilde{a}_J=0$, which gives

$$T_{\mathrm{Pr}} = T_0 + \frac{(\lambda z')^2}{4a_J'a_s}. \tag{13}$$

Thus the Pr transition temperature is enhanced due to the Cu-Pr coupling irrespective of the sign of the coupling parameter λ.

The rotation of the Cu spins in the CuO_2 plane is expressed as $\phi=\tan^{-1}(\langle S_y^{\tilde{\mathbf{Q}}}\rangle/\langle S_x^{\mathbf{Q}}\rangle)$, where $\phi=0$ corresponds to

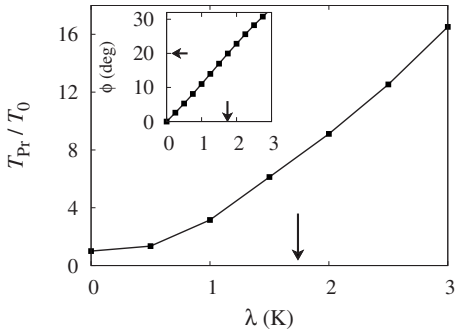

FIG. 2. Enhancement of the transition temperature, T_{Pr}/T_0, due to the coupling parameter λ. Inset shows the Cu spin-rotation angle ϕ at $T=0$ as a function of λ. The used parameter values are $\Delta=8$ K, $\Lambda=1.2$ K, $a=0.96$, and $a_s=140$. Arrows show the experimental values for ϕ and λ from Refs. 8 and 15, respectively.

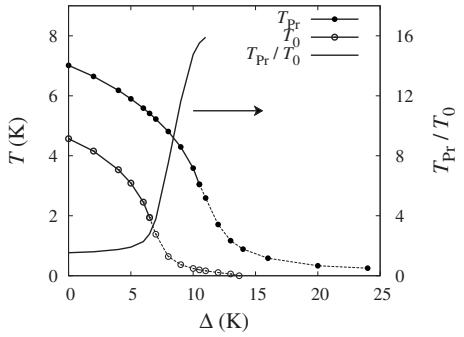

FIG. 3. Transition temperatures T_0 and T_{Pr} as a function of Δ. The parameter values are chosen as $\Lambda=1.2$ K, $\lambda=1.74$ K, and $a=0.96$. Solid line corresponds to second order while dashed line to first-order phase transition. The ratio T_{Pr}/T_0 is also shown as continuous line.

the x direction. The Cu magnetic moment is expressed as $\mu_{Cu}=g_{Cu}\mu_B[\langle S_y^{\tilde{\mathbf{Q}}}\rangle^2+\langle S_x^{\mathbf{Q}}\rangle^2]^{1/2}$, where $g_{Cu}\approx 2$ is the Cu g factor. An ordered magnetic moment of 0.66 μ_B/Cu(2) is found also for the AFI phase due to quantum fluctuations.[22] Our model includes this effect phenomenologically as this ordered magnetic moment is retained above T_{Pr} in the AFI phase.

Figure 2 shows the enhancement of the Pr transition temperature due to the Cu-Pr coupling and the corresponding Cu spin rotation angle as a function of the coupling parameter λ, calculated within the above model. We used $\Delta=8$ K and $a=0.96$ for the CEF parameters, where the latter value is obtained from the high-temperature susceptibility data[17] in $PrBa_2Cu_3O_6$. Neutron scattering found the interaction parameters as $\Lambda=1.2$ K and $\lambda=1.74$ K (Ref. 15) and an ordered Cu moment of $\mu_{Cu}=0.64$ μ_B for $x=0.35$,[8] which were used in the calculation of Fig. 2 as fix parameters. Clearly, the model accurately reproduces the $\phi=20°$ rotation of the Cu spins which was observed experimentally in Ref. 8. In addition, the model accounts for about 70% enhancement of the Pr ordering temperature with this parameter set.

The ground-state Pr magnetic moment and the enhancement of T_{Pr} strongly depends on the value of the CEF energy gap, Δ. In Fig. 3, we show the calculated T_{Pr} as a function of Δ, where we fix the interaction and CEF parameters as $\Lambda=1.2$ K, $\lambda=1.74$ K, and $a=0.96$. The value of the phenomenological parameter a_s is chosen for each Δ value so that it reproduces the experimental values $\phi=20°$ and $\mu_{Cu}=0.64$ μ_B. For small values of Δ the phase transition is second order. The transition temperatures T_0 and T_{Pr} are suppressed with increasing energy gap Δ, and the phase transition changes to first order above a critical value of Δ. Increasing further Δ, the phase transition disappears. These behaviors are due to the fact that the J_x dipole order is interaction induced within the quasitriplet subspace since the dipole operator J_x has nonvanishing matrix element only between the doublet and singlet states. Around $\Delta\sim 10$ K the ratio T_{Pr}/T_0 is considerably enhanced due to the Cu-Pr coupling.

IV. MEASUREMENT OF THE LOCAL FIELDS

Finally, we discuss the field-angle dependence of the local magnetic field acting on a Pr ion. This local field could be measured by a local magnetic probe such as, e.g., ^{89}Y using NMR (Ref. 23) or Gd^{3+} using electron spin resonance (ESR) (Ref. 24) which can be substituted into the Pr sublattice in a low concentration.

The magnetic field $\mathbf{H}_{probe}$ acting on the local magnetic probe has five different sources: exchange and dipole fields from the surrounding Cu spins, exchange and dipole fields from the surrounding Pr dipole moments, and the external magnetic field. Contributions except the external magnetic field are directed along the x direction, and we express their effect by the field h_x. We keep the field h_x fixed as the direction of the external magnetic field $\mathbf{H}$ is changed which is the situation for small values of the magnetic field.[24] For a general direction of the external magnetic field $\mathbf{H}$, we write the Hamiltonian of the local probe as

$$\mathcal{H}_{probe}=\hbar\gamma\mathbf{S}\cdot\mathbf{H}_{probe}, \tag{14}$$

where γ is the gyromagnetic ratio of the local probe and $\mathbf{S}$ is its spin (either electron or nuclear). Thus, we obtain the experimentally detected magnetic resonance shift, h_{probe} (in magnetic field units)

$$h_{probe}=(h_{res}-h_0), \tag{15}$$

where h_{res} is the resonance field and h_0 is the resonance position for the AFI phase. The external magnetic field is expressed by field angles as $\mathbf{H}/|\mathbf{H}|=[\cos\phi\sin\theta,\sin\phi\sin\theta,\cos\theta]$, and we assume that $\mathbf{S}\|\mathbf{H}$. This gives

$$h_{probe}=(h_x+H\cos\phi\sin\theta)\cos\phi\sin\theta+H(\sin\phi\sin\theta)^2+H(\cos\theta)^2. \tag{16}$$

Figure 4 shows the field angle dependence of h_{probe} by changing the direction of the magnetic field in the planes [001] and [110]. We estimate the change in h_{probe} as

$$\frac{h_{probe}[100]-h_{probe}[110]}{h_{probe}[110]-h_{probe}[001]}=\sqrt{2}-1, \tag{17}$$

which ratio can be checked in the magnetic-resonance experiments.

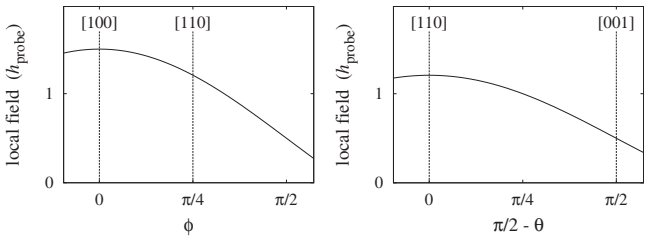

FIG. 4. Field-angle dependence of the local field h_{probe} acting on the local magnetic probe by changing the direction of the external magnetic field in the [001] (left) and [110] (right) planes with $\theta=\pi/2$ and $\phi=\pi/4$, respectively. In the plot we take the exemplifying values $h_x=1$ and $H=0.5$. The field angles are defined in the text.

V. DISCUSSION AND SUMMARY

We studied the nature of the Pr ordered phase in $PrBa_2Cu_3O_6$ in a quasitriplet CEF model of $4f^2$ electrons, where we also included the symmetry allowed coupling between the Pr and Cu ions. The reason to include Cu-Pr coupling is the Cu spin rotation observed at the Pr ordering temperature in neutron diffraction,[8,15] which has not been observed for other rare-earth $ReBa_2Cu_3O_6$ compounds. The microscopic nature of the enhanced Cu-Pr interaction remains an unresolved issue. In the $4f$ rare-earth series, the localized electrons of Pr ion tend to hybridize rather strongly with conduction electrons as in, e.g., $PrFe_4P_{12}$, which results in intriguing behavior. Besides the $Pr^{3+}4f^2$ electronic configuration, the $U^{4+}5f^2$ configuration displays also anomalous behavior in several compounds such as URu_2Si_2, where the *c-f* hybridization seems to have also a crucial role. The strong hybridization between the *f* and conduction electrons can be a reason why the Cu-*Re* coupling is much stronger in $ReBa_2Cu_3O_6$ for Re=Pr compared to the other rare-earth ions. However, to clarify the microscopic nature of the Cu-Pr coupling requires further studies which is beyond the scope of this paper.

We showed by a general symmetry analysis that there is no coupling between the Cu and Pr subsystems in phase AFI, but a coupling emerges in phase AFIII. We prove that only the AFM ordering of $J_x(J_y)$ dipole moments of Pr ions is consistent with the Cu spin rotation observed at $T=T_{\mathrm{Pr}}$ by neutron diffraction.[8,15] The interpretation of the neutron-diffraction data in Ref. 8 includes a tilting of the ordered Pr magnetic moments out of the *ab* plane. However, the presence of nonzero J_z dipole component does not follow from the general symmetry analysis as it was shown in Sec. II.

Upon identifying of the Pr order parameter, we studied the Pr ordering temperature in the Cu-Pr coupled quasitriplet CEF model by changing the interaction and CEF parameters. We found that the Cu-Pr coupling enhances the Pr ordering temperature, T_{Pr}, compared to the uncoupled ordering temperature, T_0.

By fixing the Pr-Pr and Pr-Cu interaction parameters to the values obtained by neutron diffraction,[15] and the CEF parameter to that obtained by high-temperature susceptibility measurements,[17] we found that the Pr ordering temperature is considerably enhanced due to the Cu-Pr coupling in the parameter range $\Delta\sim 8-10$ K. Namely, the enhancement of the ordering temperature is as large as $T_{\mathrm{Pr}}/T_0\sim 8-12$ in this interval. This observation explains the uniquely large ordering temperature for Re=Pr in the series $ReBa_2Cu_3O_{6+x}$.

In addition, we predicted the magnetic field angle dependence of the local magnetic field acting at a Pr site in the AFM ordered phase of the Pr ions. This can be directly compared to measured NMR or ESR spectra which detect the local magnetic field by a local magnetic probe.

Our model contains the minimal number of parameters which is required to account quantitatively for the experimental data. Given that the parameter values are assumed from independent measurements and no fit is performed, the agreement is reasonable. First, the realistic estimate $\Delta\sim 8-10$ K gives a T_{Pr} of $5-3.6$ K which is to be compared to the experimental T_{Pr} of 12 K. We note that this estimated range gives the Pr transition temperature T_0 for the uncoupled system as 0.7–0.3 K, which is close to the typical values of the ordering temperatures for other rare-earth ions such as Yb (0.35 K), Nd (0.5 K), or Dy (1 K). This fact may also indicate that the uniquely large ordering temperature for Pr arises from the Cu-Pr coupling. Second, the interval $\Delta\sim 8-10$ K is not very far from the estimate $\Delta\approx 17$ K based on the analysis of the high-temperature susceptibility data.[17] Furthermore, the estimated interval for Δ and also the splitting pattern of the quasitriplet subspace is consistent with the results of neutron scattering,[11] which found that the splitting of the ground-state quasitriplet does not exceed 2 meV above T_{Pr}, and two inelastic lines are observed at energies 1.7 and 3.4 meV at $T=5$ K in the ordered phase. Finally, for the interval $\Delta\sim 8-10$ K our CEF model gives the ordered Pr magnetic moment at low temperatures as $\mu_{\mathrm{Pr}}\sim 1.8-1.7\ \mu_{\mathrm{B}}$, which is to be compared to the observed value $\mu_{\mathrm{Pr}}=1.15\ \mu_{\mathrm{B}}$.[8] The quantitative discrepancy between the results of our model and the experimental data arises because of the simplicity of our model and minimal number of parameters.

In summary, the model we propose herein describes the main features of $PrBa_2Cu_3O_6$ system and demonstrates the importance of the Cu-Pr coupling which may be the key point to understand the anomalous behavior of this compound such as the enhancement of the Pr ordering temperature. Further studies which include also the itinerant character of $4f^2$ electrons are necessary to give an extensive description of this rather complicated system.

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