Spin Structures of Tetragonal Lamellar Copper Oxides

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The spin Hamiltonian of tetragonal lamellar antiferromagnets is shown to contain several novel anisotropies. Symmetry allows *bond-dependent* anisotropic exchange interactions, which lead to (a) interplane mean-field coupling and (b) an in-plane anisotropy which vanishes classically but arises from quantum zero point energy (QZPE). A similar QZPE involving the interplane isotropic interaction prefers collinear spins. Adding also dipolar anisotropy, the competition between all these effects explains for the first time the spin structures of many cuprates.

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The discovery of high-temperature superconductivity [1] initiated intense interest in the properties of the doped lamellar copper oxide systems. Hopefully, a step towards the understanding of the superconductivity of these systems would be to understand the simpler undoped systems, which are antiferromagnetic. In this Letter we consider two structural families of such tetragonal systems, the "123" compounds, which are isomorphic to $YBa_2Cu_3O_6$ (YBCO) [2], and the "214" compounds, isostructural to La_2CuO_4 (LCO) [3], as shown in Fig. 1.

The magnetic structure of members in the latter family has been studied for more than twenty years. Famous examples [4] include K_2NiF_4, in which the spins order perpendicular to the basal plane, and Rb_2MnF_4, where they order in that plane. The latter is also true of many cuprates, including orthorhombic LCO, and the tetragonal systems $Sr_2CuCl_2O_2$ [5], Pr_2CuO_4 [6], and Nd_2CuO_4 [6]. The magnetic properties of all these systems are very well described by an isotropic Heisenberg model in two dimensions, as demonstrated by the striking comparison between the theoretical predictions [7] for the temperature evolution of the correlation length and the corresponding experimental values at high temperatures [8–10]. However, some of the magnetic properties of these systems depend on more subtle interactions and are less well understood. In particular, the two dimensional isotropic Heisenberg model would not have a phase transition at a finite temperature. In orthorhombic LCO, the transition was explained by the finite coupling between planes and by the antisymmetric spin exchange anisotropy [3]. However, in tetragonal systems the latter anisotropy is absent, and earlier calculations gave only isotropic Heisenberg exchange [11]. The interplane coupling, which tetragonally averages out in the mean-field sense, has also not been expected to contribute. Phenomenologically, the transitions were explained to result from a crossover to an XY model, due to some small easy plane anisotropy, followed by a crossover to three dimensional long range order, due to some very weak interplanar coupling [6,8]. The easy plane anisotropy has only recently [12,13] been explained to result from the interplay of spin-orbit and Coulomb exchange interactions, and its calculated [13] magnitude was consistent with the out-of-plane spin-wave gaps in all the cuprates. However, (a) the relative ordering of spins in different planes, and (b) the low-temperature directions of the spins within the easy planes, which indicate a breaking of the in-plane XY rotational invariance, remained unexplained. The latter is particularly mysterious for the cuprates, where the spin 1/2 eliminates any single ion anisotropy. The issue becomes even more intriguing when one notes suggestions in the literature for the different spin directions in 123 and 214 systems (see Fig. 1). These issues, which we show to be interrelated, are addressed and explained in this Letter.

Topic (a) has been addressed for the case of isotropic Heisenberg interactions. In that case, for the 214 systems, there is a classical degeneracy, in that the mean field exerted by one layer on an adjacent layer vanishes for tetragonal symmetry. As first shown by Shender [14], such degeneracies are partially removed by the spin-wave quantum zero point energy (QZPE), and the lowest energy state is one with the spins collinear. Denoting the ground state spin direction at site i in the mth plane by $\hat{\mathbf{n}}_m\sigma_i$, where $\sigma_i = \pm 1$ and $\hat{\mathbf{n}}_m = \mathbf{x}\cos\theta_m + \hat{\mathbf{y}}\sin\theta_m$

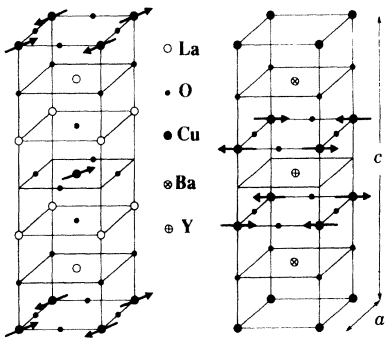

FIG. 1. Unit cells of 214 (left) and 123 (right) lamellar copper oxide tetragonal systems, with spin directions suggested for LCO [3] and YBCO [2], respectively.

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($\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are unit vectors along the Cu-Cu bonds in the basal plane), Ref. [15] showed that the relevant QZPE per spin is given by

$$E_{Z3} = -B\sum_m \cos(2\theta_m - 2\theta_{m+1}) , \quad (1)$$

where $B = C_3 J_{\rm out}^2 S/J$ to leading order in $J_{\rm out}$. Here $J_{\rm out}$ is the isotropic exchange interaction between nearest neighbors (nn) in adjacent planes (e.g., between the Cu ions in the center and in the corner of the 214 unit cell in Fig. 1), J is the average exchange within the plane, and C_3 is numerically given [15,16] to be 0.032. In LCO the *difference* between different $J_{\rm out}$'s due to the orthorhombic distortion is [3,8] 5×10^{-6} eV and [3] $J = 0.13$ eV. Using the rough estimate [17] $\Delta J_{\rm out}/J_{\rm out} \approx 10\Delta r/r \approx 0.02$ (r is the distance), this yields $J_{\rm out} \sim 2.5\times10^{-4}$ eV, and hence $B \approx 2\times10^{-9}$ eV [18]. Collinearity means that all the $\hat{\mathbf{n}}_m$'s are parallel, but there is no correlation between the σ_i's in different planes. For isotropic interactions, three dimensional long range ordering of the antiferromagnetic planes requires an even smaller energy, δE, involving either interactions J_2 between second nearest neighboring planes [16] ($\delta E \sim J_2^2/J$) or effects which are higher order in $J_{\rm out}/J$ [15] ($\delta E \sim J_{\rm out}^4/J^3$). These energies are much too small to explain the relative spin orientations of the adjacent planes in the cuprates. In this Letter we consider several new relevant energies, some of which compete with Eq. (1), and show that the relative spin orientations are determined by a delicate balance between these energies.

We now turn to question (b). Tetragonal symmetry actually allows a novel bond-dependent pairwise spin interaction between nn Cu ions in the basal plane, of the form

$$\mathcal{H}(i,j) = J_{||} S_i^{||} S_j^{||} + J_\perp S_i^\perp S_j^\perp + J_z S_i^z S_j^z , \quad (2)$$

where z, $||$ (or $\perp$) denote the directions perpendicular to the plane, and parallel (or perpendicular) to the bond connecting ions i and j in the plane, respectively. In addition to the easy plane anisotropy, which is related to $\Delta J \equiv J_{\rm av} - J_z$, where $J_{\rm av} = (J_{||} + J_\perp)/2$, Eq. (2) also contains a *bond-dependent* easy axis anisotropy, scaled by $\delta J_{\rm in} = J_{||} - J_\perp$. Although allowed by the symmetry, this anisotropy was ignored until Ref. [13] derived Eq. (2) explicitly from spin-orbit and Coulomb exchange interactions, and found $\delta J_{\rm in}$ to be of the same order as ΔJ [19]. Here we present the first analysis of Eq. (2), and also discuss similar novel interplanar bond-dependent effects. In tetragonal symmetry, a sum over all the bonds in the plane yields a mean-field energy which is rotationally invariant in the plane. Similarly, a harmonic spin-wave analysis predicts a vanishing energy of the zero wave vector in-plane mode. Our first major result concerns the modification in the spin-wave spectrum when the anisotropy scaled by $\delta J_{\rm in}$ is treated appropriately. Using the Holstein-Primakoff transformation for spin S, the linearized spin-wave spectrum for Eq. (2) is found to have two branches, with energies $\hbar\omega_\pm(\mathbf{q})$ given by

$$\frac{[\hbar\omega_\pm(\mathbf{q})]^2}{(4J_{\rm av}S)^2} = 1 - \frac{J_z c_+^2}{4J_{\rm av}} + \frac{J_z(\delta J_{\rm in})}{8J_{\rm av}^2}\cos(2\theta)c_+c_- \pm \frac{1}{4J_{\rm av}}[2(\Delta J)c_+ - (\delta J_{\rm in})\cos(2\theta)c_-] , \quad (3)$$

where $c_\pm = \cos(q_x a) \pm \cos(q_y a)$ and θ represents θ_m. Note that the dependence on θ is scaled by $\delta J_{\rm in}$.

One unusual interesting consequence of Eq. (3) is the anisotropy in $\omega(\mathbf{q})$ with respect to $\hat{\mathbf{q}}$. For example, for small q the energy of the in-plane mode is given by

$$[\hbar\omega_-(\mathbf{q})]^2 = 4(J_z + J_{\rm av})S^2a^2[J_{\rm av}q^2 - \tfrac{1}{2}(\delta J_{\rm in})\cos(2\theta)(q_x^2 - q_y^2)] . \quad (4)$$

This unusual anisotropy is quite small here since [19] $\delta J_{\rm in}/J \sim 10^{-4}$. The anisotropy in $[\hbar\omega_+(\mathbf{q})]^2$ is even smaller, being of order $\Delta J\delta J_{\rm in}\cos(2\theta)(q_x^2 - q_y^2)$.

As mentioned, the in-plane mode at $q = 0$ has zero frequency, within noninteracting spin-wave theory. However, this result is modified by spin-wave interactions. To see this, we follow Ref. [14] and consider the QZPE. Apart from a θ-independent additive constant, this is given by $E_Z = \frac{1}{2}\hbar\sum_{\mathbf{q}}[\omega_+(\mathbf{q}) + \omega_-(\mathbf{q})]$. Expanding Eq. (3) in powers of $\delta J_{\rm in}$ one obtains the θ dependence of E_Z:

$$E_Z(\theta) \approx E_Z(0) + C_1(\delta J_{\rm in})^2 S\sin^2(2\theta)/J \equiv E_Z(0) + K_{\rm in}[1 - \cos(4\theta)] . \quad (5)$$

Numerical evaluations of E_Z confirmed that Eq. (5) accurately represented the θ dependence of E_Z, as one would expect since $\delta J_{\rm in}/J$ is extremely small. These calculations gave $C_1 \approx 0.02$. Using the previous estimates of $\delta J_{\rm in}$ [19] and J we obtain $K_{\rm in} \approx 2\times10^{-12}$ eV [18]. If we neglect the coupling between planes, the θ dependence of E_Z implies that (i) the staggered magnetization picks out a direction, in this case a [100] direction, and (ii) the in-plane mode at $q = 0$ must have a nonzero energy. We estimate this energy by making a spin-wave expansion of E_Z, i.e., treating E_Z as a term in the spin-wave Hamiltonian. The result is

$$\hbar\omega_-(q=0) = 8\sqrt{2K_{\rm in}J} , \quad (6)$$

i.e., of order $|\delta J_{\rm in}|$. Taking $K_{\rm in}$ and J as above, we find that $\hbar\omega_-(q=0) \approx 10^{-5}$ eV. At present, there is no experimental estimate for this quantity. The modification of the in-plane modes due to E_Z also changes the q dependence in Eq. (3), mainly for $Jaq < \hbar\omega_-(q=0)$.

We now turn to the question of three dimensional spin ordering. Since for the cuprates ΔJ is positive and larger than $|\delta J_{\rm in}|$ [19], all the spins order antiferromagnetically in the plane. We thus consider only such ordering. The question then is what determines the orientations of the

spins within the easy plane. Choosing $\sigma = 1$ for the spin at the origin of the mth plane, the direction of that spin is along $\hat{\mathbf{n}}_m$. For the 123 structure the origins of all planes are taken to differ only in their z coordinate. For the 214 structure the origins in even and odd numbered planes are at $(0,0)$ and at $(a,a)/2$, respectively. In addition to E_Z and E_{Z3}, the spin structure is determined by three other energies (per spin). The potentially dominant energy is simply the isotropic exchange energy between nn spins in adjacent planes. Indeed, for the 123 structure this energy is dominant and causes neighboring planes to orient antiparallel to one another.

In contrast, we already mentioned that for the 214 structure this energy vanishes in the mean-field sense. Our next novel result shows that this cancellation is no longer true when one includes the anisotropic parts of the exchange tensor between nn spins in adjacent planes (e.g., the spins in the center and in a corner of the 214 cell in Fig. 1). Note that this bond lies in a (110) mirror plane. Since the midpoint of this bond is a center of inversion symmetry, the exchange tensor $J_{\rm out}$ must be symmetric [20]. The mirror plane indicates that one principal axis of $J_{\rm out}$ (denoted "$\perp$") is perpendicular to the mirror plane and the other two ("1" and "2") are in that plane, with "1" oriented at some angle ϕ (not fixed by symmetry) with respect to the tetragonal z axis perpendicular to the CuO_2 planes. Given the exchange tensor $J_{\rm out}$ for one such pair, the corresponding tensors for all other nn pairs are determined by symmetry. Summing over all nn pairs, we get the interaction energy between planes m and $m+1$ to be

$$V = 2S^2 \sin(\theta_m + \theta_{m+1})[J^{(1)}_{\rm out}\sin^2\phi + J^{(2)}_{\rm out}\cos^2\phi - J^{\perp}_{\rm out}] \equiv D\sin(\theta_m + \theta_{m+1}) \ . \quad (7)$$

To estimate the value of D, we assume that the relative anisotropy $(J^{(1)}_{\rm out} - J^{\perp}_{\rm out})/J_{\rm out}$ is similar to $\Delta J/J$. Then our estimate for $J_{\rm out}$ gives $|D| \approx 10^{-9}$ eV [18]. However, this estimate should be taken as an upper bound, since we did not consider the ϕ dependence of the square brackets in Eq. (7). For instance, for the 123 structure, symmetry dictates that $\phi = 0$ and $J^{(2)}_{\rm out} = J^{\perp}_{\rm out}$, so that $D = 0$.

The last energy to be discussed is the dipolar interaction between [21] planes m and m' which is of the form

$$V_D(m,m') = A'\cos(\theta_m - \theta_{m'}) \quad (8)$$

if planes m and m' are in registry (i.e., if they have the same origin), and is given by

$$V_D(m,m') = -A''\sin(\theta_m + \theta_{m'}) \quad (9)$$

for out of registry planes in the 214 structure. Here A' is positive and A'' is given by

$$A'' = 3g^2\mu_B^2 S^2 \sum_{j\in m'} x_{ij}y_{ij}\sigma_j/r_{ij}^5 \ , \quad (10)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, i is the origin of plane m and j is summed over all sites in plane m' [22]. We find that the sum in Eq. (10) must be carried over at least 100 shells of neighbors. For the lattice parameters of LCO ($a = 3.9$ Å, $c = 13.2$ Å) and for $m' = m+1$ the sum assumes the value 1.7×10^{-4} Å^{-3}, so that $A'' = 4.4\times10^{-9}$ eV [18]. Note that the energy of Eq. (7) can be combined with the dipolar energy by redefining the constant A'' of Eq. (9) into $A = A'' - D$. Noting the uncertainties in both the sign and size of D, the sign of A is not obvious.

Finally we discuss the spin structures one would predict on the basis of the above energies. We start with the 123 systems, which turn out to be the simplest. Here there is no frustration. The dipolar interaction given in Eq. (8) leads to an antiferromagnetic interaction between planes, which can be included in the already present antiferromagnetic Heisenberg exchange interaction. The collinearity energy E_{Z3} is also minimized by an antiferromagnetic arrangement of adjacent planes. The only remaining energy to consider, then, is the in-plane anisotropy energy of Eq. (5). This energy forces the staggered moment to lie along a [10] direction within the plane. Indeed, this structure (see Fig. 1) has been deduced from experiments [2] although the situation is not entirely clear [23].

Next we consider tetragonal 214 systems. Here the total energy is

$$E = -A\sum_m \sin(\theta_m + \theta_{m+1}) - B\sum_m \cos(2\theta_m - 2\theta_{m+1}) - K_{\rm in}\sum_m \cos(4\theta_m) \ . \quad (11)$$

The minima of E depend on the relative signs and magnitudes of A, B, and $K_{\rm in}$ ($K_{\rm in} > 0$, recall). For $|A| > 4K_{\rm in}$, the minimum occurs for $\theta_m = (A/|A|)\pi/4$ for all m if $B > K_{\rm in}$ and for $\theta_m = 0$ for m even and $(A/|A|)\pi/2$ for m odd if $B < K_{\rm in}$. Consider now $Sr_2CuCl_2O_2$. Here one has [5] $c = 15.6$ Å and $a = 3.9$ Å whence $A'' = 1.2\times10^{-9}$ eV. Since the interplanar distances are larger than in LCO, we also expect D to be smaller than estimated after Eq. (7). Thus, we expect that $A > 0$ and that both A and B dominate $K_{\rm in}$. Minimization of E then yields the spin structure shown on the left panel of Fig. 1, in agreement with the experimental suggestions [5,23].

Other 214 structures may be similarly analyzed. For instance, consider Pr_2CuO_4, which has the structure shown in Fig. 2 with the singlet ground state ion Pr^{+3}. Since the Pr ions have induced magnetic moments [6], $\mu_{\rm Pr}$, we must also consider the Cu-Pr and Pr-Pr interactions. The largest relevant energy is now the (isotropic) Cu-Pr next-nearest-neighbor (nnn) antiferromagnetic exchange [24] $J_{\rm nnn} = 4.5\times10^{-4}$ eV between, e.g., planes 1 and 3 (or 2 and 4) in the left panel of Fig. 2. These force the Pr spins in plane 3 (or 2) to be antiparallel to the nn Cu spins in plane 1 (or 4). This is also preferred by the relevant dipolar interaction, Eq. (8). Thus, if planes 1 and 4 have angles θ_m and θ_{m+1}, then planes 3 and 2 must have the angles $\theta_m + \pi$ and $\theta_{m+1} + \pi$, respectively. The whole spin structure is thus characterized by the angles θ of the CuO_2 planes. As we now show, the effective interplane coupling is dominated by the nn Cu-

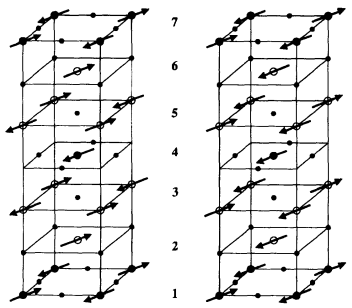

FIG. 2. Magnetic structure of Pr_2CuO_4 (left) and Nd_2CuO_4 (right) as for "214" in Fig. 1, except that open circles represent the rare earth ions.

Pr interactions, due to the small distance between these ions. The next largest energies involve the dipolar interactions of the nn Pr-Pr and interplanar nn Cu-Cu moments, given by Eq. (9). These three energies are scaled by $A''_{\text{Cu-Pr}} = 1.4 \times 10^{-7}$ eV, $A''_{\text{Pr-Pr}} = 2.8 \times 10^{-8}$ eV, and $A''_{\text{Cu-Cu}} = 8 \times 10^{-9}$ eV, respectively. Note that $A''_{\text{Pr-Pr}} < A''_{\text{Cu-Pr}}$, since $\mu_{\text{Cu}} > \mu_{\text{Pr}} = 0.08\mu_B$ [6]. Assuming that the effective D remains small, the resulting effective term in Eq. (11) now has $A = A''_{\text{Cu-Cu}} - 2A''_{\text{Cu-Pr}} + A''_{\text{Pr-Pr}} < 0$. Next consider the analog of Eq. (1), caused by the Pr-Cu exchange interactions, J_{nn}, which average to zero in the mean-field sense. Although the geometry here is not exactly the same as in Ref. [15], and there are short range differences, we still expect the corresponding B to be of order $C_3 J_{\text{nn}}^2 S/J$. Taking $J_{\text{nn}} > J_{\text{nnn}}$ gives $B > 4 \times 10^{-8}$ eV. Thus both A and B dominate K_{in}, and minimization of Eq. (11) then yields the apparently observed [6] structure shown in Fig. 2 [23].

Now what can we say about the other observed structures, such as the various phases of Nd_2CuO_4 [6]? The low-temperature phase of this material is shown on the right panel in Fig. 2, and it contradicts everything said in the previous paragraph. Possible explanations could be as follows: (a) If this state is dominated by the exchange interactions between planes 1 and 3 (or 2 and 4), then these would have to be ferromagnetic. (b) A small compression along the axis of the staggered moments would lead to an appropriate net mean-field coupling between adjacent planes. However, this works only if J_{nnn} is very small, given the small upper limit on such a distortion [6]. (c) The parameter D for the nn Cu-Pr might be sufficiently large to make A in Eq. (11) both negative and also large enough to overcome the other energies. We hope these considerations will help in the resolution of this puzzle.

In summary, we have identified several novel sources of anisotropy in the antiferromagnetic tetragonal lamellar perovskite structures. These include the in-plane QZPE given by Eq. (5), and the interplanar mean-field anisotropy given by Eq. (7). In addition, we allowed the dipolar energy to depend on the relative ordering of the spins in different planes [Eq. (8) or (9)], and added the Shender-like interplanar QZPE of Eq. (1). The combined effects of all these energies led to a consistent explanation of several observed spin structures. We expect these ideas to work for many other similar systems.

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[1] J. G. Bednorz and K. A. Muller, Z. Phys. B **64**, 189 (1986).
[2] J. Rossat-Mignod *et al.*, in *Selected Topics in Superconductivity*, edited by L. C. Gupta and M. S. Multani (World Scientific, Singapore, 1993), p. 265.
[3] T. Thio *et al.*, Phys. Rev. B **38**, 905 (1988).
[4] R. J. Birgeneau *et al.*, Phys. Rev. B **1**, 2211 (1970).
[5] D. Vaknin *et al.*, Phys. Rev. B **41**, 1926 (1990).
[6] M. Matsuda *et al.*, Phys. Rev. B **42**, 10098 (1990).
[7] S. Chakravarty *et al.*, Phys. Rev. B **39**, 2344 (1989); D. P. Arovas and A. Auerbach, Phys. Rev. B **38**, 316 (1988).
[8] B. Keimer *et al.*, Phys. Rev. B **46**, 14034 (1992).
[9] M. Greven *et al.*, Phys. Rev. Lett. **72**, 1096 (1994).
[10] R. J. Birgeneau, Phys. Rev. B **41**, 2514 (1990).
[11] For example, L. Shekhtman *et al.*, Phys. Rev. B **47**, 174 (1993).
[12] F. Barriquand and G. A. Sawatzky (to be published).
[13] T. Yildirim, A. B. Harris, O. Entin-Wohlman, and A. Aharony (to be published).
[14] E. F. Shender, Sov. Phys. JETP **56**, 178 (1982).
[15] T. Yildirim, A. B. Harris, and E. F. Shender (to be published).
[16] E. Rastelli *et al.*, J. Phys. Condens. Matter **2**, 8935 (1990).
[17] D. Bloch, Ann. Phys. (Paris) **1**, 93 (1966). See p. 119.
[18] For numerical estimates we replace S by the average Cu z component of spin 0.2, or the corresponding z component of moment $\mu_{\text{Cu}} = 0.4\mu_B$.
[19] According to Ref. [13] $\Delta J/J$ is positive and larger in magnitude than $\delta J_{\text{in}}/J$, but both quantities are of order 10^{-4}. Here, $J = (J_z + J_\perp + J_\parallel)/3 = 0.13$ eV.
[20] T. Moriya, Phys. Rev. **120**, 91 (1960).
[21] The dipolar energy of a square-lattice antiferromagnet with the staggered moment confined to the plane of the lattice is independent of the orientation of staggered moment. This energy does favor spin directions perpendicular to the CuO_2 plane [e.g., C. Pich and F. Schwabl, Phys. Rev. B **47**, 7957 (1993)], but we neglect it since we find it to be less than 10% of the energy $\sim \Delta J$ which favors the spins to be in the CuO_2 plane.
[22] The role played by the dipolar energy was already considered in Ref. [5]. However, these authors *assumed* a collinear spin structure, with θ_m allowed to be only $\pi/4$ or $5\pi/4$.
[23] In the comparisons with experiments one should keep in mind that there is always some difficulty in determining the direction of the staggered moment within the plane, due to the occurrence of domains. See G. Shirane, Acta Crystallogr. **12**, 282 (1959).
[24] J_{nnn}, defined via $\mathcal{H} = J_{\text{nnn}}\mu_{\text{Pr}}\mu_{\text{Cu}}/\mu_B^2$, is deduced from Fig. 7 and Eq. (3) of Ref. [6].