Na content dependence of superconductivity and the spin correlations in $Na_xCoO_2 \cdot 1.3H_2O$

2006 J. Phys.: Condens. Matter 18 L63

(http://iopscience.iop.org/0953-8984/18/5/L02)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) L63–L70 doi:10.1088/0953-8984/18/5/L02

LETTER TO THE EDITOR

Na content dependence of superconductivity and the spin correlations in $Na_xCoO_2{\cdot}1.3H_2O$

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Received 3 January 2006
Published 20 January 2006
Online at stacks.iop.org/JPhysCM/18/L63

Abstract

We report systematic measurements using the ^{59}Co nuclear quadrupole resonance (NQR) technique on the cobalt oxide superconductors $Na_xCoO_2{\cdot}1.3H_2O$ over a wide Na content range $x = 0.25$–0.34. We find that T_c increases with decreasing x but reaches a plateau for $x \leqslant 0.28$. In the sample with $x \sim 0.26$, the spin–lattice relaxation rate $1/T_1$ shows a T^3 variation below T_c and down to $T \sim T_c/6$, which unambiguously indicates the presence of line nodes in the superconducting (SC) gap function. However, for larger or smaller x, $1/T_1$ deviates from the T^3 variation below $T \sim 2$ K even though the T_c ($\sim$4.7 K) is similar, which suggests an unusual evolution of the SC state. In the normal state, the spin correlations at a finite wavevector become stronger upon decreasing x, and the density of states at the Fermi level increases with decreasing x, which can be understood in terms of a single-orbital picture suggested on the basis of LDA calculation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The layered cobalt oxides Na_xCoO_2 have attracted much attention in recent years, because of a rich variety of orders competing for the ground state. For $x = 0.75$, the material shows a large thermoelectric power [1, 2], while the $x = 0.5$ compound is a charge ordered insulator with $T_{CO} = 50$ K [3]. The magnetic properties are different for different Na contents [3–5]. On the side with x larger than 0.5, the DC susceptibility shows a Curie–Weiss temperature (T) variation, while on the low-x side the susceptibility is T independent [3]. Most interestingly, superconductivity with $T_c \sim 4.5$ K emerges around $x = 0.3$ when water molecules are

Table 1. Characterizations of the samples.

Br amount	Na content x	c-axis length (Å)	a-axis length (Å)	T_c (K)
5 X	0.34	19.50	2.822	2.65
10 X	0.32	19.62	2.822	3.60
10 X [11]	0.31	19.59	2.819	3.70
20 X	0.28	19.73	2.817	4.75
40 X	0.25	19.80	2.817	4.70
100 X	0.26	19.79	2.815	4.60

intercalated in between the Co layers [6]. It has been reported that T_c can be tuned by varying x in the range of $0.25 \leqslant x \leqslant 0.38$ [7].

One of the unsettled issues on the superconductivity is the symmetry of the gap function. Theoretically, a chiral$(d + id)$ superconducting state was first proposed on the basis of the RVB scenario [8–10]. In a previous study, we found that the spin–lattice relaxation rate $1/T_1$ shows no coherence peak below T_c, and follows a T^n variation with $n = 2.2$–1 at low T [11]. This suggests that the superconductivity is of non-BCS type, but it has been pointed out that the data are insufficient to distinguish between some exotic states [12–14]. It has been shown that both chiral and pure d-wave states in the presence of disorder [12, 13], or an odd-frequency s-wave state [14] can be compatible with such T-variation of T_1. Since identification of the gap function is the first step toward the understanding of the superconductivity, more work is needed.

Another issue is how the electron correlations in the normal state evolve with doping, which should help in understanding the mechanism for the superconductivity. In the octahedral crystal electric field environment, two e_g orbitals of Co are located much higher in energy above t_{2g} orbitals. The local density approximation (LDA) band calculation shows that [15–17], among the three t_{2g} orbitals, the a_{1g} ($3d_{3z^2-r^2}$, where z-axis is the threefold rotation axis) orbit lies higher in energy than the remaining two e'_g orbitals. If one takes this picture [8, 9], then the Co^{4+} state without Na has one electron in the a_{1g} orbital (spin 1/2), with the e'_g orbitals fully occupied. This single-orbital situation resembles the undoped cuprates; adding Na dopes electrons into the a_{1g} orbital. In contrast, multiple-band models were also proposed [18, 19], which draw similarities to the manganese oxides, another important class of strongly correlated materials.

In this letter, we address the above two issues by studying the evolution of the system with doping using the NQR (nuclear quadrupole resonance) technique. We present intensive data on the superconducting and the normal states over a wide range of Na content.

2. Experimental results and discussion

The $Na_xCoO_2{\cdot}yH_2O$ powder [20] was synthesized following [6]. The precursor of $Na_{0.75}CoO_2$ was immersed in the Br_2/CH_3CN solution to de-intercalate Na. The amount of Br_2 is listed in table 1, where X means the theoretical value necessary to remove all the Na. The Na content of the final product was determined by the ion coupled plasma method. X-ray diffraction indicates that the samples are single phase except the 5 X ($x \sim 0.34$) and 10 X ($x \sim 0.32$) samples in which minor secondary phases are present. The c-axis elongates as the Na content decreases, in agreement with a previous report [7]. T_c was determined from the ac susceptibility and the $1/T_1$ measurements. The previously reported sample [11] was made with 10 X Br amount in a separate run and turned out to have an $x \sim 0.31$. All other samples were made in the same

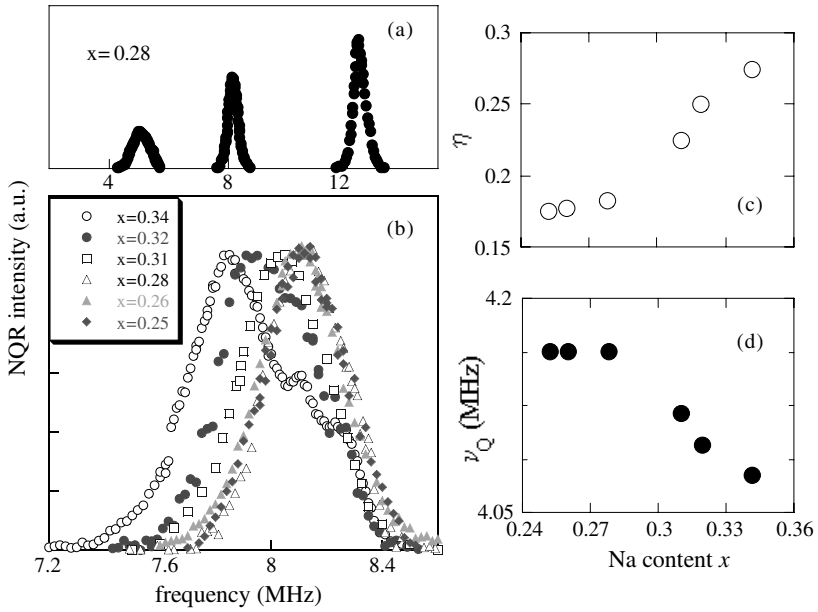

Figure 1. (a) ^{59}Co NQR spectra for the sample of $x \sim 0.28$; (b) the line shape of the $\pm 3/2 \leftrightarrow \pm 5/2$ transition for various Na contents; (c), (d) Na content dependences of the asymmetric parameter η and ν_Q, respectively.

run. ^{59}Co NQR measurements were carried out by using a phase-coherent spectrometer. The nuclear magnetization decay curve is excellently fitted to the theoretical curves [24], with a unique T_1 component.

Figure 1(a) shows a typical example of the three NQR transition lines arising from the nuclear spin $I = 7/2$ of ^{59}Co. Figure 1(b) shows the $\pm 3/2 \leftrightarrow \pm 5/2$ transition line for various Na contents. Firstly, the peak frequency increases as x decreases down to $x = 0.28$. Analysis of three transition lines allows us to find that ν_Q increases as the Na content decreases down to $x = 0.28$, but the asymmetry parameter η decreases monotonically with decreasing Na content, as seen in figures 1(c) and (d), respectively. Here ν_Q and η are defined as $\nu_Q \equiv \nu_z = \frac{3}{2I(2I-1)h} e^2 Q \frac{\partial^2 V}{\partial z^2}$, $\eta = |\nu_x - \nu_y|/\nu_z$, with Q being the nuclear quadrupole moment and $\frac{\partial^2 V}{\partial \alpha^2} (\alpha = x, y, z)$ being the electric field gradient at the position of the nucleus [21]. The decrease of ν_Q with increasing x is consistent with doping electrons into the A_{1g} orbit [23]. Secondly, for the 5 X ($x \sim 0.34$) and 10 X ($x \sim 0.32$) samples, there appear multiple peaks for the transition. However, the additional peaks with smaller amplitude are not due to the minor impurity phase detected in the x-ray chart. Rather, we find that $1/T_1$ measured in different peaks differs only by 10% in magnitude and shows the identical temperature variation; a clear decrease was seen below T_c. These peaks may have arisen from the ordering of Na ions [22] which are located above and below Co. More detailed discussion will be published elsewhere [23]. We note in passing that the multiple peaks seen in the $\pm 3/2 \leftrightarrow \pm 5/2$ transition are not resolvable in the $\pm 5/2 \leftrightarrow \pm 7/2$ transition.

Figure 2 shows the temperature dependence of the quantity $1/T_1T$ for various x. All measurements were made at the $\pm 3/2 \leftrightarrow \pm 5/2$ transition. For the 5 X and 10 X samples, $1/T_1$ was measured at the main peak shown in figure 1(b). Two trends can be seen in figure 2. First, the absolute value increases with decreasing x. Second, $1/T_1T$ increases upon lowering

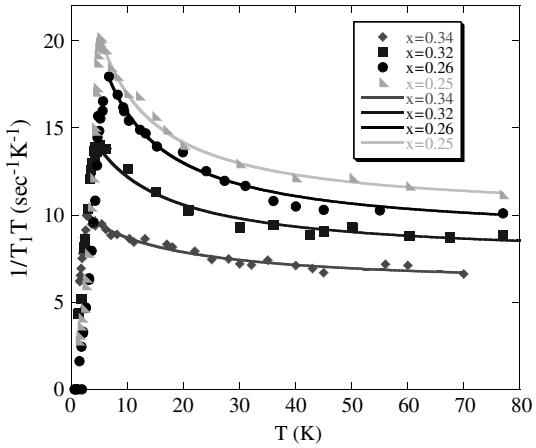

Figure 2. The quantity $1/T_1T$ as a function of temperature for various Na contents. The curves are fits to $1/T_1T = (1/T_1T)_0 + C/(T+\theta)$, with resulting parameter $C = 75$, 77, 111 and 123 s^{-1} for $x = 0.34$, 0.32, 0.26 and 0.25, respectively. The values of $(1/T_1T)_0$ and θ are plotted in figure 3.

T, indicating the importance of spin correlations; the smaller the x the steeper the increase, indicating that the spin correlations become stronger as x is reduced.

What is the nature of the spin correlations? One good way to tell is through inspection of the Knight shift, which measures the spin susceptibility and, unlike the bulk susceptibility, is not affected by the presence of magnetic impurities. In a superconducting single crystal with $x \sim 0.3$, we found that the shift is T invariant from T_c up to $T = 120$ K [30], which is in good agreement with the report of Ning *et al* [31]. These results rule out the possibility of ferromagnetic spin fluctuations with wavevector $q = 0$, since in that case the Knight shift would follow the temperature dependence of $1/T_1T$ because both of them would be dominated by the susceptibility at wavevector $q \sim 0$.

The results thus indicate that the spin fluctuations peak at finite wavevector. The most likely candidate is antiferromagnetic (AF) correlations [8–10, 32], although its detailed q-dependence awaits clarification by future experiments, in particular neutron scattering. Below we analyse our data in terms of AF correlations, in an attempt to quantify the discussion. In a general form, $1/T_1T$ is written as $1/T_1T = \sum_q A_q^2 \chi''(q,\omega)/\omega$ in the $\omega \to 0$ limit, where A_q is the hyperfine coupling constant, and $\chi''(q,\omega)$ is the imaginary part of the q-dependent, dynamical susceptibility. If one assumes that there is a peak around the AF wavevector Q, then one may have the following approximation: $1/T_1T = (1/T_1T)_{AF} + (1/T_1T)_0$. Here $(1/T_1T)_0$ denotes the contribution from wavevectors other than Q, which usually is dominated by the uniform susceptibility χ_0. For the AF contribution, we use the formula for a two-dimensional nearly antiferromagnet, namely, $(1/T_1T)_{AF} = \frac{C}{T+\theta}$ [33]. We find that such a model fits the data quite successfully, as depicted by the curves in figure 2. The resulting fitting parameters are shown in figure 3. Note that a small value of θ means that a system is close to the AF instability ($\theta = 0$). The enhancement of the spin correlation (decrease of θ) with decreasing x, as is the case in doped copper oxide high-T_c superconductors, can be naturally understood in the single-orbital picture [8, 9] described earlier. In contrast, the multiple-band theory predicts Na-content-insensitive, ferromagnetic spin correlations [19].

Turning to the quantity $(1/T_1T)_0$, its increase with decreasing x can be attributed to the increase of density of states (DOS) at the Fermi level. This result is consistent with the LDA band calculation which found that the dominant Fermi surface is a *hole-like* one and that the

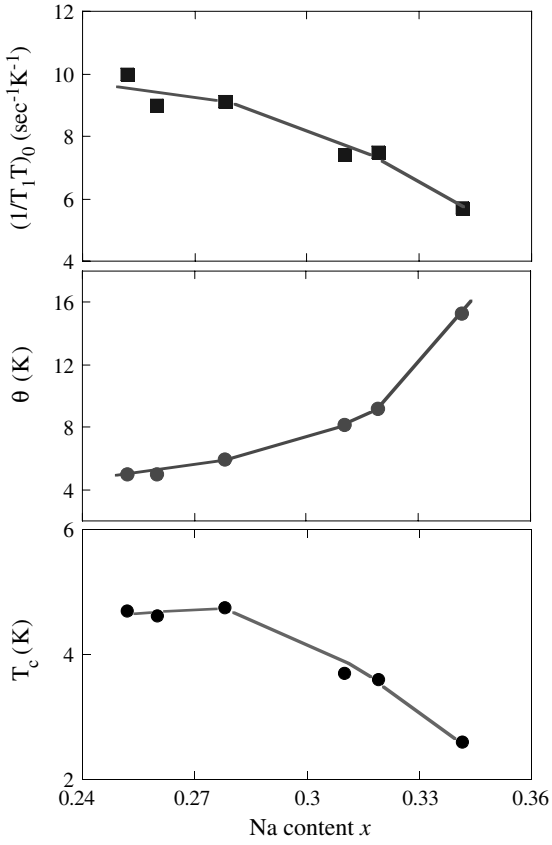

Figure 3. Various parameters obtained in this study plotted as a function of Na content, x. The curves are guides to the eyes.

DOS increases as the electron number is reduced [16, 34]. This aspect is different from the case of doped cuprates where the DOS decreases with decreasing carrier density. We summarize our results in figure 3. As x decreases from 0.34, T_c increases, but reaches a plateau of ∼4.7 K for $x \leqslant 0.28$. Our results for high value of x are in good agreement with the report by Schaak *et al* [7]. A plateau has also been reported recently by Chen *et al* and Milne *et al* [25, 26]. It is interesting to note that as the parameter θ decreases and C increases, namely, as the electron correlation becomes stronger, T_c increases.

Next, we turn to the superconducting state. As can be seen already in figure 2, no coherence peak was seen just below T_c in all samples, irrespective of Na content and/or T_c value. However, the low-T behavior is sample dependent. We first show in figure 4 the results for the sample with $x \sim 0.26$. It can be seen that $1/T_1$ follows a T^3 variation down to the lowest temperature measured ($\sim T_c/6$). This result indicates unambiguously that there exist line nodes in the gap function. As we noted in previous publications [11, 27], the gap function with line nodes generates an energy- (E-) linear DOS at low E which results in a T^n ($n = 3$) dependence of $1/T_1$. In the previous sample, $1/T_1$ did not follow an exact T^3 variation and became proportional to T below $T \sim T_c/2$, [11]. It has been proposed that many exotic superconducting states can be compatible with the data [12–14]. Calculations incorporating impurity/disorder scattering showed that a $d_{x^2-y^2} + id_{xy}$ state which has a full

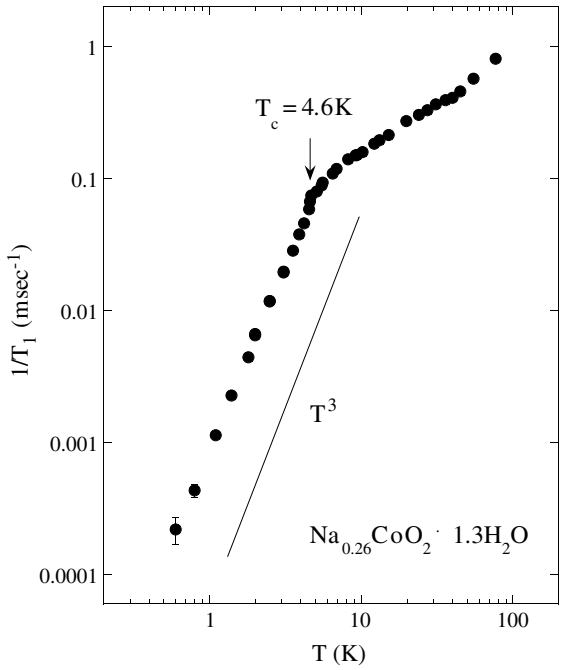

Figure 4. Temperature dependence of $1/T_1$ for the sample of $x = 0.26$. The arrow indicates T_c. The straight line depicts the T^3 variation.

gap is more consistent with the previous data [12]. Our present result completely rules out the $d_{x^2-y^2}+id_{xy}$ state proposed by the t–J model in an isotropic triangular lattice [8–10, 28]. Also, the odd frequency state proposed [14] is gapless [35, 36], and is incompatible with our finding in the $x = 0.26$ sample. However, if anisotropy of the t term is incorporated, the theories could be compatible with our experimental results. In fact, it has been recently shown that a small anisotropy in t (10–20%) lifts the degeneracy between $d_{x^2-y^2}$ and d_{xy} states, leading to a stabilization of a pure d-wave state [29].

In other samples with either larger or smaller x, however, $1/T_1$ deviates from the T^3 relation below $T = 2.0$ K. To see this more clearly, we plot the T-dependence of $1/T_1$ for all samples in figure 5. In the inset of the figure is shown the normalized $1/T_1$ by its value at $T = T_c$ against the reduced temperature. What is responsible for the deviation from the T^3 variation in samples with x either larger or smaller than 0.26? Disorder or impurity is an unlikely candidate, since the samples with $x \sim 0.28$ and $x \sim 0.25$ have very similar or even higher T_c and NQR line-width to the $x \sim 0.26$ sample. Clearly, this unprecedented property deserves further investigation, both experimentally and theoretically. Meanwhile, low-lying excitations due to nearby competing orders may be a possible candidate. For larger x, it is known that charge ordering [3, 22] occurs. The Na order could also give rise to the anisotropy of the hopping integral t mentioned earlier. For smaller x, on the other hand, it has been proposed that different charge/magnetic order may occur at $x = 1/4$ [37].

3. Conclusion

In conclusion, we have presented intensive ^{59}Co-NQR measurements on the cobalt oxide superconductors $Na_xCoO_2{\cdot}1.3H_2O$ over a wide Na content range $x = 0.25$–0.34. We find that

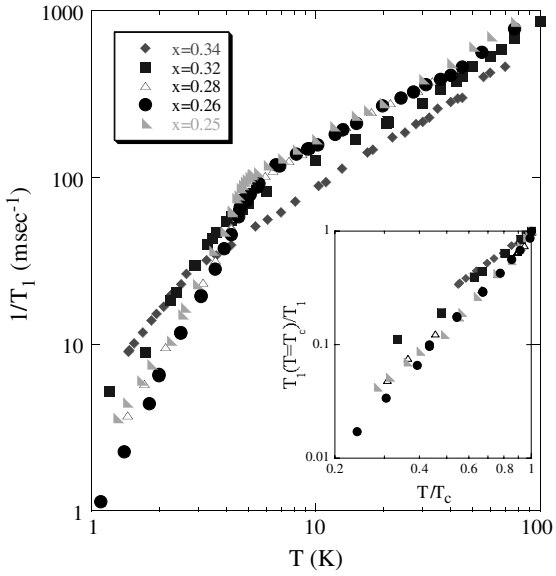

Figure 5. A comparison of the temperature dependence of $1/T_1$ in the superconducting state for various samples with different Na content. The inset shows the normalized $1/T_1$ by its value at $T = T_c$ against the reduced temperature.

T_c increases with decreasing x but reaches a plateau for $x \leqslant 0.28$. In the superconducting state, the spin–lattice relaxation rate $1/T_1$ shows a T^3 variation down to $T \sim T_c/6$ for $x \sim 0.26$, which indicates unambiguously the presence of line nodes in the superconducting gap function. For both larger and smaller x, however, $1/T_1$ deviates from the T^3 dependence even through the T_c value is similar. This unprecedented finding shows the richness of the physics of this new class of superconductors, and any pertinent theory must explain this peculiar property. In the normal state, the temperature dependence of $1/T_1T$ indicates that the spin correlations at finite wavevector become stronger upon decreasing x, while the DOS increases. This aspect is different from the case of doped cuprates but can be understood in terms of a single-orbital picture suggested on the basis of LDA calculation.

We thank Y Sun for x-ray chart analysis and G Baskaran, Y Fuseya, H Harima, Y Kitaoka, G Khaliullin, C T Lin, K Miyake, M Ogata and Y Yanase for helpful discussions. This work was supported in part by research grants from MEXT, NSF, the TLL Temple Foundation, the John and Rebecca Moores Endowment, and the DoE.

References

[1] Terasaki I, Sasago Y and Uchinokura K 1997 *Phys. Rev.* B **56** R12685
[2] Wang Y, Rogado N, Cava R J and Ong N P 2003 *Nature* **423** 425
[3] Foo M L *et al* 2004 *Phys. Rev. Lett.* **92** 247001
[4] Barnhard C *et al* 2004 *Phys. Rev. Lett.* **93** 167003
[5] Boothroyd A T *et al* 2004 *Phys. Rev. Lett.* **92** 197201
[6] Takada K *et al* 2003 *Nature* **422** 53
[7] Schaak R E *et al* 2003 *Nature* **424** 527
[8] Baskaran G 2003 *Phys. Rev. Lett.* **91** 097003
[9] Wang Q H, Lee D H and Lee P A 2004 *Phys. Rev.* B **69** 092504

[10] Ogata M 2003 *J. Phys. Soc. Japan* **72** 1839
[11] Fujimoto T, Zheng G Q, Kitaoka Y, Meng R L, Cmaidalka J and Chu C W 2004 *Phys. Rev. Lett.* **92** 047004
[12] Bang Y *et al* 2003 *Phys. Rev.* B **68** 212504
[13] Wang Q H and Wang Z D 2004 *Phys. Rev.* B **69** 092502
[14] Johnees M D *et al* 2004 *Phys. Rev. Lett.* **93** 097005
[15] Singh D J 2000 *Phys. Rev.* B **61** 13397
[16] Zou L J, Wang J L and Zeng Z 2004 *Phys. Rev.* B **69** 132505
[17] Kunes J, Lee K W and Pickett W E 2004 *Phys. Rev.* B **70** 045104
[18] Khaliullin G, Koshibae W and Maekawa S 2004 *Phys. Rev. Lett.* **93** 176401
[19] Yanase Y, Mochizuki M and Ogata M 2005 *J. Phys. Soc. Japan* **74** 430
[20] Lorenz B *et al* 2003 *Phys. Rev.* B **68** 132504
[21] Abragam A 1961 *The Principles of Nuclear Magnetism* (London: Oxford University Press)
[22] Zandbergen H W *et al* 2004 *Phys. Rev.* B **70** 024101
[23] Matano K and Zheng G Q 2006 in preparation
[24] Chepin J and Ross J H 1991 *J. Phys.: Condens. Matter* **3** 8103
[25] Chen D P *et al* 2004 *Phys. Rev.* B **70** 024506
[26] Milne C J *et al* 2004 *Phys. Rev. Lett.* **93** 247007
[27] Zheng G Q *et al* 2001 *Phys. Rev. Lett.* **86** 4664
[28] Liu B, Liang Y and Feng S 2005 *Commun. Theor. Phys.* **43** 1127
[29] Watanabe T, Yokoyama H, Tanaka Y, Inoue J and Ogata M 2004 *Preprint* cond-mat/0411711
[30] Zheng G Q, Matano K, Chen D P and Lin C T 2006 The Knight shift contains substantial contribution from the spin susceptibility, at press
[31] Ning F L *et al* 2004 *Phys. Rev. Lett.* **93** 237201
[32] Gasparovic G *et al* 2005 *Preprint* cond-mat/0508158
[33] Moriya T, Ueda K and Takahashi Y 1990 *J. Phys. Soc. Japan* **59** 2905
[34] Zhang P, Luo W, Crespi V, Cohen M L and Louie1 S 2004 *Phys. Rev.* B **70** 085108
[35] Mazin I I and Johannes M D 2005 *Preprint* cond-mat/0506536
[36] Fuseya Y, Kohno H and Miyake K 2003 *J. Phys. Soc. Japan* **72** 2914
[37] Baskaran G 2003 *Preprint* cond-mat/0306569

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J. Phys.: Condens. Matter **18** (2006) 9307 PII: S0953-8984(06)18114-X

Erratum

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Gou-qing Zheng 2006 *J. Phys.: Condens. Matter* **18** L63–70

Received February 2006
Published February 2006
Online at stacks.iop.org/JPhysCM/18/9307
doi:10.1088/0953-8984/18/40/

The unit on the y axis of figure 5 should be (sec^{-1}).

