Evidence for a large magnetic heat current in insulating cuprates

M. Hofmann[1], T. Lorenz[1], K. Berggold[1], M. Grüninger[1], A. Freimuth[1], G.S. Uhrig[2], and E. Brück[3]
[1] *II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*
[2] *Institut für Theoretische Physik, Universität zu Köln, 50937 Köln, Germany*
[3] *Van der Waals-Zeemann Laboratorium, University of Amsterdam, 1018 XE Amsterdam, The Netherlands*
(Dated: February 2, 2008)

The in-plane thermal conductivity k of the two-dimensional antiferromagnetic monolayer cuprate $Sr_2CuO_2Cl_2$ is studied. Analysis of the unusual temperature dependence of k reveals that at low temperatures the heat is carried by phonons, whereas at high temperatures magnetic excitations contribute significantly. Comparison with other insulating layered cuprates suggests that a large magnetic contribution to the thermal conductivity is an intrinsic property of these materials.

There is growing experimental evidence that spin excitations may contribute significantly to the heat current in low-dimensional spin systems. This seems to be well established for one-dimensional (1D) systems[1,2,3,4,5]. For example, in the insulating spin-ladder material $Sr_{14-x}Ca_xCu_{24}O_{41}$ a large magnetic contribution k_m to the thermal conductivity k can be derived from a pronounced double-peak structure of k along the ladder direction[2,4]. The situation is less clear in two-dimensional (2D) spin systems. These are, however, of particular importance due to their relevance for high-temperature superconductivity[6,7]. A double-peak structure comparable to that in 1D systems is found in the in-plane thermal conductivity of insulating 2D cuprates such as La_2CuO_4 (LCO) and $YBa_2Cu_3O_6$ (YBCO) (Ref. 8,9,10). This may indicate a sizable magnetic contribution to the heat current at high temperatures[8]. However, the phononic thermal conductivity k_{ph} may show a double-peak structure also, as a result of pronounced (resonant) scattering in a narrow temperature range. Such scattering may arise from the presence of local magnetic excitations, as was recently shown for the 2D spin-dimer system $SrCu_2(BO_3)_2$ (Ref. 11), or it may arise from the presence of soft phonon modes[9]. The latter was suggested for LCO and YBCO, in which soft modes e.g. associated with tilt distortions of the CuO polyhedra are known to be present[9,12]. An additional complication arises from a strong sensitivity of the double-peak structure to light oxygen doping[9].

A material of particular interest in this context is $Sr_2CuO_2Cl_2$ (SCOC). It is structurally very similar to LCO: It contains CuO_2-layers as in LCO, but the out-of-plane oxygen ions at the apices of the CuO_6-octahedra are replaced by Cl and La by Sr. The material has several advantages compared to LCO and YBCO (see e.g. Ref. 6): (1) SCOC does not exhibit any distortion from tetragonal symmetry down to at least 10K so that there is no structural instability associated with soft tilting modes. (2) Because of the absence of tilt distortions the magnetic properties are simpler than those of LCO. For example, there is no Dzyaloshinski-Moriya exchange interaction. Thus, SCOC is believed to represent the best realization of a two-dimensional square-lattice $S = 1/2$ Heisenberg antiferromagnet. (3) In contrast to LCO and YBCO, SCOC cannot be doped easily with charge carriers.

In this paper we present measurements of the in-plane thermal conductivity k of SCOC. We identify a double-peak structure from a pronounced high-temperature shoulder around 230 K. Analysis of these data and a comparison to LCO and YBCO shows that it is very unlikely that the double peak structure arises from anomalous phonon damping due to scattering on soft lattice modes or magnetic excitations. The data indicate instead a large magnetic thermal conductivity at high temperatures as an intrinsic feature of the insulating 2D cuprates.

We studied a single crystal of $Sr_2CuO_2Cl_2$ of rectangular form ($1 \times 3 \times 4$ mm^3) with the short direction along the crystallographic c axis. It was grown by the traveling-solvent floating zone method. The thermal conductivity was measured with the heat current within the CuO_2 planes by a conventional steady-state method using a differential Chromel-Au+0.07%Fe-thermocouple. Typical temperature gradients were of the order of 0.2 K. The absolute accuracy of our data is restricted by uncertainties in the sample geometry whereas the relative accuracy is of the order of a few %.[13].

We show in Fig. 1 the in-plane thermal conductivity of SCOC as a function of temperature. We identify a maximum at ≈ 30 K and a shoulder at high temperatures around 230K. The pronounced low-temperature maximum of k indicates a high crystal quality. We note that k is independent of a magnetic field (≤ 8 Tesla) applied within the CuO_2 planes perpendicular to the heat current. For comparison we show in Fig. 1 the in-plane thermal conductivity of a single crystal of LCO measured by Nakamura et al.[8]. These data also reveal a double-peak structure. The absolute value of k at the low-temperature maximum is smaller than in SCOC. One reason may be that LCO is more sensitive to defects, resulting e.g. from excess oxygen, which introduces lattice defects and hole doping and thus reduces the mean free path of the heat-carrying excitations.

Both compounds, SCOC and LCO, are antiferromagnetic insulators. In an insulator the heat is usually carried by phonons. The typical behavior of k_{ph} of a crystalline insulator is shown by the solid lines in Fig. 1. These curves represent fits to the low-temperature maximum of k (fitted below about 50 K) of SCOC and LCO using the standard Debye model for the thermal conduc-

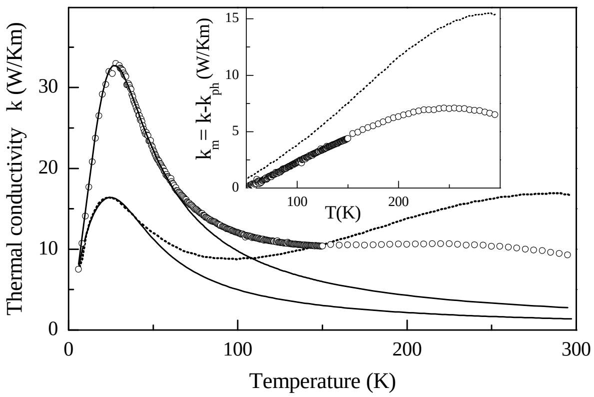

FIG. 1: In-plane thermal conductivity $k(T)$ of $Sr_2CuO_2Cl_2$ (circles) and La_2CuO_4 (dotted line; data from Nakamura et al.[8]). Solid lines: fits to k_{ph} using the Debye model[11,14]. The fitting parameters for $Sr_2CuO_2Cl_2$ (La_2CuO_4) are: $D/10^{-17}$s = 3.4 (2.6); $P/10^{-43}\mathrm{s}^3 = 0.15$ (21); $U/10^{-30}\mathrm{s}^2/\mathrm{K} = 1.0$ (2.2); $u = 4.9$ (4.4). The point defect scattering (P) is smaller in SCOC. Inset: $k_m = k - k_{ph}$ for $Sr_2CuO_2Cl_2$ (circles) and La_2CuO_4 (dotted line) (see text).

tivity of acoustic phonons[11,14]:

$$k_{ph} = \frac{k_B^4 T^3}{2\pi^2 \hbar^3 v_{ph}} \int_0^{\Theta_D/T} \tau(x,T) \frac{x^4 e^x}{(e^x - 1)^2} dx \ . \qquad (1)$$

Here Θ_D is the Debye temperature and v_{ph} the sound velocity. Due to the lack of experimental data for SCOC we use for both compounds the values reported for LCO ($\Theta_D \approx 385$ K[15]; $v_{ph} \approx 5.2 \cdot 10^3$ m/s[16]). ω is the phonon frequency, $x = \hbar\omega/k_B T$, and $\tau(x,T)$ is the phonon relaxation time given by

$$\tau^{-1} = \frac{v_{ph}}{L} + D\omega^2 + P\omega^4 + UT\omega^3 \exp\left(\frac{\Theta_D}{uT}\right) .$$

The four terms refer to the scattering rates for boundary scattering, scattering on planar defects, on point defects, and phonon-phonon Umklapp scattering, respectively. $L \approx 1$mm is the sample length, and D, P, U, and u are fitting constants. The low-temperature data are described very well by these fits. The fit parameters are given in the caption of Fig. 1. The decrease of k_{ph} at high temperatures is due to phonon-phonon Umklapp scattering.

For several reasons it is very unlikely that the high-temperature increase of k is due to conventional heat transport by phonons: (1) The contribution to k from acoustic phonons, as described above, decreases at high temperatures. (2) The contribution of optical phonons to the heat current is usually much smaller than that of acoustic phonons, even in compounds with a very large number of atoms in the unit cell[5,17], so that heat transport by optical phonons is very unlikely to cause the high-temperature maximum. (3) The out-of-plane thermal conductivity k_c of LCO behaves as the in-plane thermal conductivity k at low temperatures, but k_c shows no indication of a high-temperature maximum[8]. Such strongly temperature dependent anisotropy is not expected for purely phononic heat conduction.

Additional phonon scattering, active in a narrow temperature range close to the minimum of k, may in principle cause a double-peak structure. However, resonant scattering on local magnetic excitations as in $SrCu_2(BO_3)_2$ (Ref. 11) cannot be the correct explanation in the present case: In the 2D square-lattice cuprates the dispersion of magnetic excitations ranges from ≈ 0 to $2J/k_B \gtrsim 2000$ K (J is the in-plane exchange constant) so that there is no reason that scattering on magnetic excitations should be most pronounced in a narrow temperature interval around 100 K.[11,19] Note, in particular, that in the 2D cuprates scattering on magnetic excitations should not disappear above the Néel-temperature T_N, because the relevant energy scale is set by $J \gg T_N$ (see below). Additional phonon damping from scattering on soft lattice modes as suggested in Ref. 9 is also unlikely as a cause of the double peak: (1) There are no lattice instabilities in SCOC, rendering this mechanism unimportant for this material. (2) The double-peak structure is also present in the tetragonal low-temperature phase of Eu-doped LCO, in which no soft tilting modes should be present either[10]. (3) The absence of a double-peak structure of k_c in LCO (Ref. 8) implies that anomalous phonon scattering would have to be active only for k. Such strong anisotropy of the phonon-phonon scattering is not expected. Finally, note that the finding $k_c < k$ in LCO (Ref. 8) provides evidence against any scattering scenario as a cause of the double peak structure: for such scattering, if active only for k, but absent for k_c, implies $k < k_c$, in contradiction to the experimental results.

The data of Fig. 1 (in particular $k > k_c$) are most naturally explained, if an additional channel of heat transport for the in-plane thermal conductivity is present. In an undoped insulating 2D Heisenberg antiferromagnet with an electronic gap $\gtrsim 1.5$ eV, the only candidate for heat transport next to phonons are magnetic excitations. Their thermal conductivity k_m adds to that of the phonons, i.e. $k = k_{ph} + k_m$. In order to extract k_m from the data we subtract k_{ph} as obtained from the fit of the low-temperature maximum. Note that k_m cannot be obtained at $T \lesssim 100$K in this way, because Eq. 1 was fitted to the *total* k below 50 K. Remarkably, k_m is of comparable magnitude (roughly of the order 10 W/Km) in both compounds (see inset Fig. 1). The maximum of k_m is at ≈ 245 K in SCOC and at ≈ 285 K in LCO.

Is a magnetic contribution of this size reasonable? We estimate k_m using the kinetic equation in 2D[14]:

$$k_m = \frac{1}{2} c_m v_m \ell_m \, . \qquad (2)$$

Here c_m is the magnetic specific heat and ℓ_m the mean free path of the magnetic excitations. The velocity v_m of long-wavelength spin waves is $v_m^{\mathrm{SCOC}} \approx 1.06 \cdot 10^5$ m/s

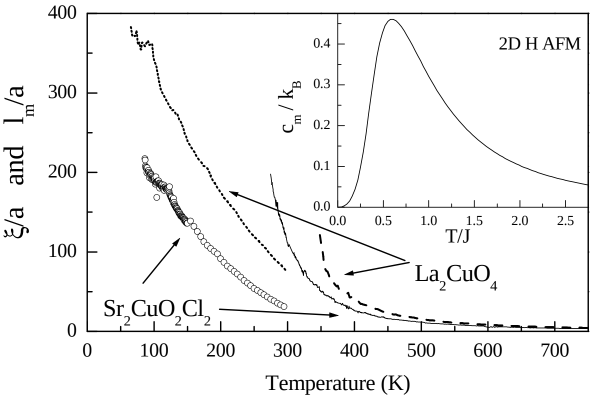

FIG. 2: Magnetic mean free path $\ell_m(T)/a$ (circles: $Sr_2CuO_2Cl_2$; dotted line: La_2CuO_4) as extracted from the data shown in Fig. 1 (see text), and in-plane magnetic correlation length $\xi_m(T)/a$ (solid line: $Sr_2CuO_2Cl_2$; dashed line: La_2CuO_4) as obtained from neutron scattering[7]. Here, $a \simeq 3.9$ Åis the lattice constant. Inset: Specific heat c_m/k_B of a $S = 1/2$ square-lattice Heisenberg antiferromagnet (see appendix).

and $v_m^{\mathrm{LCO}} \approx 1.16 \cdot 10^5$ m/s, which is obtained from $v_m = \sqrt{8}SZ_cJa/\hbar$. Here Z_c is the Oguchi correction.[20] Values of J for various 2D cuprates are given in Table I. Note that v_m is much larger than v_{ph}, as a result of $J \gg k_B\Theta_D$. For the specific heat c_m we use the theoretical result shown in the inset of Fig. 2, which comes from the extrapolation of the high-temperature series for the partition sum (see appendix). The maximum is $c_{\max} = 0.4612(5)Nk_B$ at $k_BT_{\max} = 0.5956(1)J$. Given v_m, c_m, and using k_m as shown in Fig. 1 we obtain an estimate of $\ell_m(T)$ using Eq. (2). ℓ_m decreases strongly with increasing temperature (Fig. 2). At room temperature, $\ell_m/a \approx 30$ for SCOC and ≈ 75 for LCO. These values are not excessively large – much larger values of ℓ_m have been found in one-dimensional spin systems[2,3,4] – rendering a magnetic contribution to the heat current in SCOC and LCO very plausible.

For a better understanding of k_m it is instructive to discuss the magnetic correlations in the quasi-2D cuprates, in particular, the in-plane magnetic correlation length $\xi_m(T)$. In a 2D antiferromagnet long-range order with $\xi_m = \infty$ is restricted to T=0. With increasing temperature spin-flips (or magnons) are excited, which reduce ξ_m by breaking the long-range correlation. In the quasi-2D materials considered here, the finite magnetic ordering temperature T_N is determined by the *inter*-plane interaction[6,7], which is much weaker than the in-plane exchange interaction J, so that $k_BT_N \ll J$ (see Tab. I). In the ordered state at $T < T_N$, $\xi_m = \infty$. For $T > T_N$, ξ_m is still large because of the large J. We show $\xi_m(T)$ of SCOC and LCO as inferred from magnetic neutron scattering[7] in Fig. 2. Above T_N, ξ_m is indeed much larger than the lattice constant. However, ξ_m decreases strongly with increasing temperature, approximately according to[7] $\xi_m(T) \simeq \exp(2\pi J/k_BT)$.

	T_H (K)	T_N (K)	J/k_B (K)	J/k_BT_H
$YBa_2Cu_3O_6$	200	> 400	1125	5.6
$Sr_2CuO_2Cl_2$	245	260	1220	5.0
La_2CuO_4	285	320	1390	4.9

TABLE I: Position T_H of the high-temperature maximum of k_m, Neel-temperature T_N, in-plane magnetic exchange coupling constant J, and the ratio J/k_BT_H for three insulating 2D cuprates. Note that J/k_BT_H is very similar in all three compounds. T_N is from Refs. 6,7,32. The values of J are derived from two-magnon Raman scattering and infrared bimagnon-plus-phonon absorption data[24,33], where the Oguchi correction has been taken into account.[20] The data for k in YBCO and LCO are from Refs. 9 and 8, respectively.

From these considerations we may draw several conclusions for the magnetic heat current: (1) We expect that k_m is determined by the large in-plane exchange interaction J and not by the inter-plane interactions. Therefore, no significant anomaly of k_m is expected at T_N. (2) At least above T_N the heat-carrying magnetic excitations are not the familiar collective excitations of a magnetically ordered state (i.e. conventional magnons), but rather magnetic excitations (of triplet character) in a spin-liquid state. Note, however, that also at $T < T_N$ the nature of the magnetic excitations of the 2D cuprates is under intensive debate[24,25,26,27,28]. (3) The strong, exponential decrease of ξ_m above T_N suggests a similar decrease of $\ell_m(T)$. This would explain, why the maximum of k_m occurs at a temperature much lower than that of c_m: the increase of $c_m(T < T_{max})$ is overcompensated by the strong decrease of $\ell_m(T)$. Note, however, that the results on $Sr_{14-x}Ca_xCu_{24}O_{41}$ show that in a spin-liquid ℓ_m may be significantly larger than ξ_m.[2,4]

A double-peak structure of k has also been reported for the insulating bilayer compound $YBa_2Cu_3O_6$.[9] As in LCO one observes pronounced anisotropy, i.e. k_c does not show a high-temperature maximum. Given the existence of a large k_m in the monolayer cuprates LCO and SCOC, the high-temperature maximum of YBCO is also likely to be of magnetic origin. This is consistent with the systematic variation of the temperature T_H of the high-temperature maximum of k with J for the three different insulating cuprates as shown in Tab. I.

The data in Fig. 1 show that the high-temperature maximum is more pronounced in LCO than in SCOC. A related observation is the weak high-temperature anomaly of k in Pr_2CuO_4.[29] In view of their rather similar magnetic properties one would expect a similar behavior of k_m in these compounds.[30] However, doping with mobile charge carriers[9,10] or static impurities[10,31] influences the high-temperature maximum strongly. In particular, the high-temperature maximum in YBCO depends in a non-monotonic way on the oxygen concentration[9]. Thus the different behavior of k_m might result from the fact that LCO and YBCO can easily be doped with charge carriers via variation of the oxygen content, whereas this is not possible in SCOC.

Further experiments with a detailed control of the charge-carrier concentration could clarify this issue.

In summary, the in-plane thermal conductivity of $Sr_2CuO_2Cl_2$ shows an unusual temperature dependence with a pronounced shoulder at high temperatures, similar to the behavior found for La_2CuO_4[8] and $YBa_2Cu_3O_6$.[9] There is no structural instability in $Sr_2CuO_2Cl_2$. Moreover, scattering on magnetic excitations is not restricted to a narrow temperature interval around the minimum of k in these compounds. It is therefore unlikely that the double peak structure arises from strong damping of the phononic heat current by resonant scattering on soft lattice modes or magnetic excitations. The data rather indicate a large magnetic contribution to the heat current as an intrinsic property of the 2D cuprates.

We acknowledge useful discussions with M. Braden, W. Hardy, A.P. Kampf, V. Kataev, D.I. Khomskii, and G.A. Sawatzky. This work was supported by the Deutsche Forschungsgemeinschaft in SFB 608 and in SP 1073. A.F. acknowledges support by the VolkswagenStiftung.

APPENDIX

To deduce $c(T)$ from the high-temperature series[21] this series is converted in a series for the entropy s in the energy per site e (Ref. 22). The extrapolations are stabilized by information on the ground state energy $e_0 = -0.669437(5)$ (Ref. 23), the maximum entropy $s = \ln 2$, and the expected low-energy power law $s(e) \propto (e - e_0)^{2/3}$. For the latter, Padé approximants are applied to $s'(e)/s(e) - 2/(3(e - e_0))$ (Dlog Padé approximation). Very good results are obtained (reliable error estimate 10^{-2} from comparing diagonal to non-diagonal Padé approximants). The result shown in the inset of Fig. 2 (error 10^{-3}) is obtained by approximating

$$\left[\frac{(e - e_0)s'(e)}{s(e)} - \frac{2}{3}\right] \ln\left(\frac{e - e_0}{1 - e_0}\right), \qquad (3)$$

which allows for multiplicative logarithmic corrections, yielding $c(T) \propto T^2(A + \ln^{-\gamma}(1/T))$ with $A = 0$ and $\gamma = 1.05(5)$. We do not, however, exclude a small finite value of A as found in spin-wave theory.

[1] Y. Ando, J. Takeya, D.L. Sisson, S.G. Doettinger, I. Tanaka, R.S. Feigelson, and A. Kapitulnik, Phys. Rev. B **58**, R2913 (1998).

[2] A. V. Sologubenko, K. Gianno, H.R. Ott, U. Ammerahl, and A. Revcolevschi, Phys. Rev. Lett. **84**, 2714 (2000).

[3] A.V. Sologubenko, K. Gianno, H.R. Ott, A. Vietkine, and A. Revcolevschi, Phys. Rev. B **64**, 054412 (2001).

[4] C. Hess, C. Baumann, U. Ammerahl, B. Büchner, F. Heidrich-Meisner, W. Brenig, and A. Revcolevschi, Phys. Rev. B **64**, 184305 (2001).

[5] T. Lorenz, M. Hofmann, M. Grüninger, A. Freimuth, G.S. Uhrig, M. Dumm, and M. Dressel, Nature 418, 614 (2002).

[6] D.C. Johnston, *Normal-State Magnetic Properties of Single-Layer Cuprate High-Temperature Superconductors and Related Materials*, in Handbook of Magnetic Materials Vol. **10**, K.H.J. Buschow (ed.) (Elsevier 1997).

[7] M.A. Kastner, R.J. Birgeneau, G. Shirane, and Y. Endoh, Rev. Mod. Phys. **70**, 897 (1998) and references therein.

[8] Y. Nakamura, S. Uchida, T. Kimura, N. Motohira, K. Kishio, and K. Kitazawa, Physica C **185**, 1409 (1991).

[9] J. L. Cohn, C. K. Lowe-Ma, and T. A. Vanderah, Phys. Rev. B **52**, R13134 (1995).

[10] C. Hess, Ph.D. thesis, University of Cologne, ISBN 3-89820-378-6, 2002.

[11] M. Hofmann, T. Lorenz, G.S. Uhrig, H. Kierspel, O. Zabara, A. Freimuth, H. Kageyama, and Y. Ueda, Phys. Rev. Lett. **87**, 047202 (2001).

[12] L. Pintschovius and W. Reichardt, in *Physical Properties of High Temperature Superconductors*, D.M. Ginsberg (Ed.), World Scientific, Singapore, 1992, Vol. 5.

[13] To obtain reproducible data the samples should not be exposed to air, because SCOC is strongly hygroscopic.

[14] R. Bermann, *Thermal Conduction in Solids* (Clarendon Press, Oxford, 1976).

[15] A. Junod, in *Physical Properties of High Temperature Superconductors*, D.M. Ginsberg (Ed.), World Scientific, Singapore, 1989, Vol. 2.

[16] T. Suzuki, T. Fukase, S. Wakimoto, and K. Yamada Physica B **284**, 479 (2000).

[17] G.A. Slack, Sol. Stat. Phys. **34**, 1 (1979).

[18] J.L. Cohn, J. Supercond. **8**, 457 (1995).

[19] B. C. Sales, M. D. Lumsden, S. E. Nagler, D. Mandrus, and R. Jin, Phys. Rev. Lett. **88**, 095901 (2002).

[20] T. Oguchi, Phys. Rev. **117**, 117 (1960).

[21] J. Oitmaa and E. Bornilla, Phys. Rev. B **53**, 14228 (1996).

[22] B. Bernu and G. Misguich, Phys. Rev. B **63**, 134409 (2001).

[23] A.W. Sandvik, Phys. Rev. B **56**, 11678 (1997).

[24] M. Grüninger, D. van der Marel, A. Damascelli, A. Erb, T. Nunner, and T. Kopp, Phys. Rev. B **62**, 12422 (2000).

[25] C.-M. Ho, V.N. Muthukumar, M. Ogata, and P.W. Anderson, Phys. Rev. Lett. **86**, 1626 (2001).

[26] G. Aeppli, S.M. Hayden, P. Dai, H.A. Mook, R.D. Hunt, T.G. Perring, F. Dogan, phys. stat. sol. b **215**, 519 (1999).

[27] A.W. Sandvik and R.R.P. Singh, Phys. Rev. Lett. **86**, 528 (2001).

[28] R.B. Laughlin, Phys. Rev. Lett. **79**, 1726 (1997).

[29] A.V. Sologubenko, D.F. Brewer, G. Ekosipedidis, and A.L. Thomson, Physica B **263-264**, 788 (1999)

[30] We do not expect a pronounced influence of the Dzyaloshinski-Moriya interaction present in LCO on k_m.

[31] A.N. Taldenkov, A.V. Inyushkin, and T.G. Uvarova, Czech. J. Phys. **46**, 1169 (1996).

[32] J. Rossat-Mignod, L.P. Regnault, M.J. Jurgens, C. Vettier, P. Burlet, J.Y. Henry, and G. Lapertot, Physica B **163**, 4 (1990).

[33] J. Lorenzana and G.A. Sawatzky, Phys. Rev. B **52**, 9576 (1995).