Magnetic susceptibility in the normal state: A tool to optimize T_c within a given superconducting oxide system

C. Allgeier*
Sektion Physik, Universität München, Schellingstrasse 4, W-8000 München 40, Germany and Walther-Meissner-Institut, Walther-Meissner-Strasse 8, W-8046 Garching, Germany

J. S. Schilling
Department of Physics, Washington University, Campus Box 1105, One Brookings Drive, St. Louis, Missouri 63130-4899
(Received 28 April 1993)

We compare the static magnetic susceptibilities of $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{6+y}$, $Bi_2Sr_{1.6}La_{0.4}CuO_{6+y}$, $Bi_2Sr_2CaCu_2O_{8+y}$, $Tl_2Ba_2CuO_{6+y}$, $Tl_2Ba_2CaCu_2O_{8+y}$, and $Tl_2Ba_2Ca_2Cu_3O_{10+y}$ as a function of the oxygen content. The main results are that (1) the spin susceptibility in the normal state χ_s is primarily determined by the CuO_2 layers, (2) the Meissner fraction increases markedly with the transition temperature T_c, and (3) for samples with the optimum value of T_c, χ_s correlates linearly with the calculated band-structure density of states at the Fermi energy. We also discuss how the value of the magnetic susceptibility in the normal state can be used to optimize T_c within a given compound system.

I. INTRODUCTION

A good deal of experimental research on high-temperature superconductors has been directed toward establishing correlations between properties in the normal and superconducting states. Such studies are of particular value since they have the potential to give information on the interactions responsible for the formation of the superconducting state and to test contending theoretical models. The systematic variation of the fundamental properties for as many high-T_c superconductors as possible is desirable in order to be able to separate those correlations which are common to all oxide superconductors from those which are peculiar to only a few. The application of well-defined hydrostatic or uniaxial pressure to a sample is a particularly clean way to vary its properties.[1] Alternatively, the charge carrier density in the CuO_2 planes can be varied by either chemical substitution or the progressive removal of one or more of the constituents, such as oxygen.[2–16] It is the latter method which we apply in the present work.

Although for experimental reasons the magnetic susceptibility of the superconducting oxides has been relatively little studied, its measurement yields information not only on the superconducting state (Meissner or shielding fraction, coherence length, London penetration depth, properties of the vortex lattice, etc.) but also on such normal-state properties as the density of electron states at the Fermi surface $N(E_F)$ or spin fluctuations. In this paper we attempt to analyze in a consistent way the results of detailed studies by our group, some of which have already been published, of the temperature-dependent normal-state magnetic susceptibility of selected superconducting oxides under variation of the oxygen concentration. These results for variable oxygen content are then compared to those from substitution experiments on $La_{2-x}Sr_xCuO_4$.[2,3]

II. EXPERIMENT

The present measurements were carried out on polycrystalline samples of the single-layer systems $Bi_2Sr_{1.6}La_{0.4}CuO_{6+y}$ (Ref. 11) and $Tl_2Ba_2CuO_{6+y}$,[14] the double-layer systems $YBa_2Cu_3O_{6+y}$,[9] $Bi_2Sr_2CaCu_2O_{8+y}$,[14] and $Tl_2Ba_2CaCu_2O_{8+y}$,[13] and the triple-layer system $Tl_2Ba_2Ca_2Cu_3O_{10+y}$.[10] A detailed description of the sample preparation procedure is given in Refs. 9–14.

Structure studies carried out with standard x-ray powder diffractometry reveal that, with a single exception, all specimens are single phase; the $Tl_2Ba_2Ca_2Cu_3O_{10+y}$ sample contains an admixture of $\sim 20\%$ of $Tl_2Ba_2CaCu_2O_{8+y}$.[10] The hole content of our samples, which we define for simplicity as $p \equiv 2y$, is varied by changing the oxygen content y. The absolute oxygen concentration of $YBa_2Cu_3O_{6+y}$, $Bi_2Sr_{1.6}La_{0.4}CuO_{6+y}$, and $Bi_2Sr_2CaCu_2O_{8+y}$ was determined by iodometric titration; the change in oxygen content was inferred from the weight loss of the sample, as described below. For the $Tl_2Ba_2CuO_{6+y}$ specimen we estimate the absolute value of y from a comparison with neutron-scattering data.[14] For the two- and three-layer thallium compounds the oxygen content y was neither measured nor varied.

All measurements of the magnetic susceptibility were carried out in the same manner using a Faraday magnetometer described elsewhere.[12,14] This system allows a controlled reduction of the oxygen content of the samples by heating the specimen in high vacuum and measuring the weight loss of the oxygen driven off. The removal of oxygen is verified using a mass spectrometer. The static magnetic susceptibility in the normal and superconducting states can thus be measured on a single sample *in situ* at different oxygen contents. X-ray diffractometry at room temperature carried out after the magnetometer

studies revealed no alterations in the crystal structure or impurity phase peaks.

III. RESULTS

In Fig. 1, the Meissner fraction (ratio of the transition height for field-cooled to zero-field-cooled data) for various oxide systems at variable oxygen concentrations is plotted versus the superconducting transition temperature T_c; both quantities are normalized to their maximal values within each compound system. For a particular compound, all measurements were made on a single specimen at fixed orientation to the magnetic field, thus eliminating uncertainties due to demagnetization effects. Since the transition width varies significantly, we use in Fig. 1 the saturated flux expulsion values at 4 K. The results for $La_{2-x}Sr_xCuO_4$ are taken from Dover *et al.*[17] Although the data in Fig. 1 scatter somewhat, the trend is obvious: the Meissner fraction increases with the transition temperature. We suggest that this trend reflects increased vortex pinning for suboptimal values of T_c.

Lee, Klemm, and Johnston[18] have shown that the normal-state magnetic susceptibility $\chi(T)$ of the superconducting oxides is altered for temperatures below $\sim 2T_c$ by the onset of diamagnetic superconducting fluctuations. Since T_c lies near 100 K for the majority of oxides studied here, to accurately characterize $\chi(T)$ it is essential to extend the temperature range of the measurements of the normal-state susceptibility to temperatures well above room temperature. The present measurements were thus carried out to as high a temperature as possible without loss of oxygen, in some cases as high as 900 K. As an example, we show in Fig. 2 the measured susceptibility of $Tl_2Ba_2CuO_{6+y}$ and $Bi_2Sr_2CaCu_2O_{8+y}$; these data are published in more detail in Ref. 14.

An inspection of Fig. 2 reveals two characteristic trends followed by the magnetic susceptibility of the high-temperature superconductors: (1) the susceptibility decreases continuously with decreasing hole content $p=-2y$, and (2) the transition temperature T_c deduced from the Meissner measurements takes on its maximal value at that hole content where the temperature dependence of the normal-state susceptibility is most nearly flat. This behavior is also observed in $La_{2-x}Sr_xCuO_4$,[2,3] $Bi_2Sr_{2-x}La_xCuO_{6+y}$,[11,15] and $YBa_2Cu_3O_{6+y}$,[7-9] where the hole content is given by $p=x+2y$, and indicates a correlation between $d\chi/dT$ and T_c for the superconducting oxides. It is well known that the superconducting transition temperature of the oxides appears to pass through a bell-shaped curve $T_c(p)$ as a function of the hole content p. As we pointed out in Ref. 14, for suboptimal hole concentrations to the left of the $T_c(p)$ maximum, the slope $d\chi/dT$ is positive, at the optimal hole concentration T_c takes its maximum value and $d\chi/dT \approx 0$, whereas for above optimal hole content $d\chi/dT < 0$.

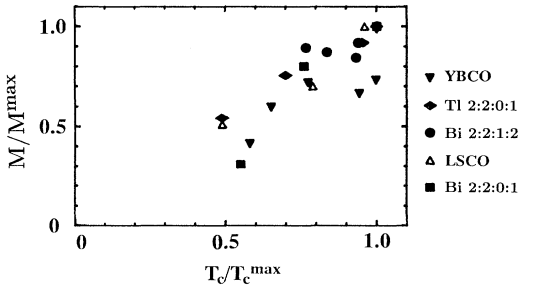

FIG. 1. Normalized Meissner fraction versus transition temperature normalized to its maximum value within each compound. A magnetic field of 1–2 mT is applied. The abbreviations are LSCO for $La_{2-x}Sr_xCuO_{4+y}$, YBCO for $YBa_2Cu_3O_{6+y}$, Tl 2:2:0:1 for $Tl_2Ba_2CuO_{6+y}$, Bi 2:2:0:1 for $Bi_2Sr_{1.6}La_{1.4}CuO_{6+y}$, and Bi 2:2:1:2 for $Bi_2Sr_2CaCu_2O_{8+y}$.

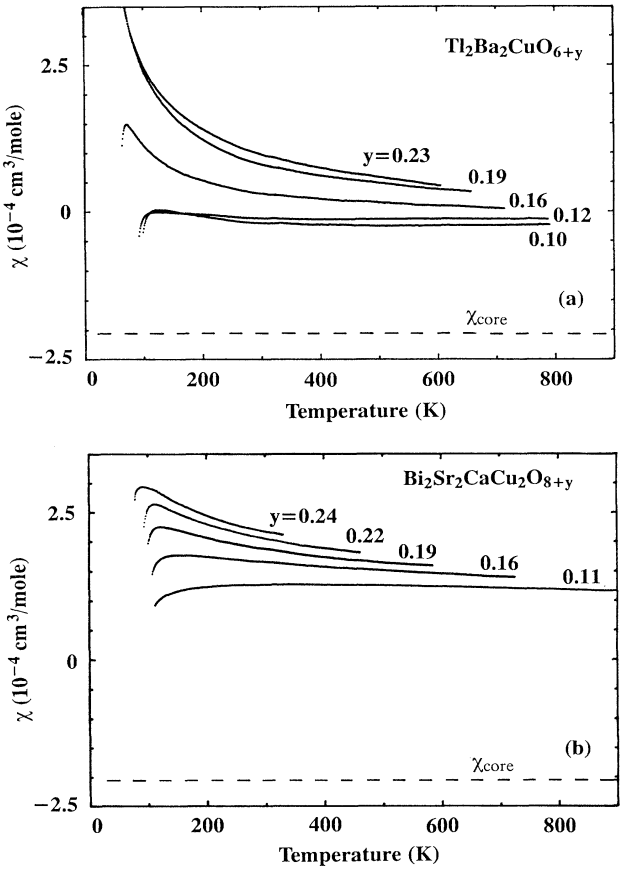

FIG. 2. Total measured magnetic susceptibility per mole of (a) $Tl_2Ba_2CuO_{6+y}$ and (b) $Bi_2Sr_2CaCu_2O_{8+y}$ at 5.7 T versus temperature for various oxygen contents y. The diamagnetism of the core ions is indicated by a dashed line; the change in core diamagnetism with oxygen content here is negligible.

In Fig. 3 we plot as a function of T_c the magnetic susceptibility at 300 K, a temperature high enough to practically eliminate possible influences of Curie-tail-like and/or superconducting fluctuation contributions. The values of the susceptibility shown in this figure have already been corrected for the temperature-independent core diamagnetism estimated from Ref. 19 and listed in Table I below. For comparison the results of Torrance *et al.*[2] on $La_{2-x}Sr_xCuO_4$ are included in Fig. 3. The

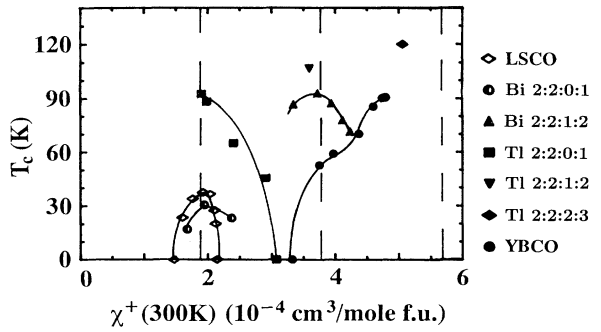

FIG. 3. Transition temperature T_c versus magnetic susceptibility χ^+ per mole formula unit at 300 K after correction for χ_{core}, i.e., $\chi^+(300\text{ K})=\chi(300\text{ K})-\chi_{\text{core}}$. The abbreviations have the same meaning as in Fig. 1. In addition, Tl 2:2:1:2 represents $Tl_2Ba_2CaCu_2CaCu_2O_{8+y}$ and Tl 2:2:2:3 represents $Tl_2Ba_2Ca_2Cu_3O_{10+y}$.

measured susceptibilities of $Tl_2Ba_2CaCu_2O_{8+y}$ and $Tl_2Ba_2Ca_2Cu_3O_{10+y}$ contain sizable Curie-Weiss contributions[20] which presumably arise from paramagnetic impurity phases and/or disorder effects. The Curie-Weiss contributions[20] for these two compounds have been subtracted off from the data shown in Fig. 3.

Several important results are seen in Fig. 3. First, no simple correlation seems to exist between the magnitude of the susceptibility and the transition temperature. Although the systems with one CuO_2 layer per formula unit possess quite comparable values of the susceptibility, their transition temperatures can differ by nearly a factor of 3. Second, the susceptibilities of most systems are centered around integral multiples of $\Delta\chi\simeq 1.9\times10^{-4}$ cm^3/mol, as indicated by the dashed lines. This indicates that the paramagnetic susceptibility per formula unit increases approximately linearly with the number of CuO_2 layers in the unit cell, a result which can only be understood if the paramagnetic contribution originates predominantly from the CuO_2 planes. $YBa_2Cu_3O_7$ fits very well into this picture too, although this is not immediately evident from an inspection of Fig. 3. Possessing two CuO_2 layers plus a fully occupied CuO chain, the value of the susceptibility for $YBa_2Cu_3O_7$ lies in between the values expected for the two- and three-layer compounds. However, using the analysis given below to correct for the paramagnetic contributions from the chains, the susceptibility of $YBa_2Cu_3O_7$ is found to map correctly onto the dashed line for the two-layer compounds.

IV. DISCUSSION

We will now give a brief discussion of the various contributions to the susceptibility of the normal state. In the absence of magnetic impurity contributions or disorder effects,[21] which can lead to Curie or Curie-Weiss tails at low temperature, the normal-state magnetic susceptibility of the superconducting oxides can be written as the sum over core, Van Vleck, and spin terms:

$$\chi=\chi_{\text{core}}+\chi_{\text{VV}}+\chi_{\text{spin}}\ . \tag{1}$$

The Landau diamagnetism can be neglected here as we will see later. As mentioned above, χ_{core}, the temperature-independent diamagnetism of the closed inner ionic orbitals can be estimated using the tables in Ref. 19. The Van Vleck paramagnetism originates from ions with nonclosed shells and is mainly responsible for the anisotropy of the susceptibility observed in measurements on single crystals or oriented powder.[5,22,23] Since this contribution is due to transitions between the Cu $3d_{xy}$, Cu $3d_{xz,yz}$, and the Cu $3d_{x^2-y^2}$ orbitals whose energies are separated by several electron volts [$\Delta E=1.7$–2.5 eV for $YBa_2Cu_3O_{6+y}$ (Ref. 24)], χ_{VV} is expected to be temperature independent in the experimental temperature range. From a comparison of susceptibility results with NMR data,[22] Lee and Johnston[25] determined for $YBa_2Cu_3O_7$ a value of $\chi_{\text{VV}}=+0.43\times10^{-4}$ cm^3/mol f.u. per CuO_2 layer. We obtain a very similar value (0.48×10^{-4} cm^3/mol f.u. per CuO_2 layer) for $Bi_2Sr_2CaCu_2O_{8.16}$ by a comparison of the data for $\chi(300$ K) in Fig. 2(a) with ^{17}O NMR measurements of Trokiner *et al.*[26] Thus, it appears that a value of $\chi_{\text{VV}}\simeq+0.43\times10^{-4}$ cm^3/mol f.u. per CuO_2 layer is a good first approximation for all high-temperature superconductors. This is supported by the close similarity in the environment of the CuO_2 layers in high-T_c superconductors, resulting in a similar anisotropy in the normal-state

TABLE I. Pauli susceptibility of the specimens with the maximal T_c estimated from the measured values at 300 K. The calculated core diamagnetism from Ref. 19 and the assumed Van Vleck paramagnetism are also listed. T_c is determined from the Meissner transition. The asterisks indicate units of 10^{-4} cm^3/mol.

Compound	T_c (K)	χ_{core}*	χ_{VV}*	χ_{Pauli}*	Reference
$La_{1.85}Sr_{0.15}CuO_{4+y}$	37.5	−0.98	0.43	1.49	2
$YBa_2Cu_3O_7$	91.0	−1.93	1.32	3.66	21
$YBa_2Cu_3O_7$	91.0	−1.93	1.32	3.47	This work
$Bi_2Sr_{1.6}La_{0.4}CuO_{6.29}$	30.6	−1.65	0.43	1.51	This work
$Bi_2Sr_2CaCu_2O_{8.16}$	92.8	−2.06	0.86	2.86	This work
$Tl_2Ba_2CuO_{6.10}$	92.5	−2.09	0.43	1.47	This work
$Tl_2Ba_2CaCu_2O_{8+y}$	106.8	−2.52	0.86	2.73	This work
$Tl_2Ba_2Ca_2Cu_3O_{10+y}$	120.0	−2.95	1.29	3.77	This work

susceptibility irregardless of whether the material is a superconducting metal, a nonsuperconducting metal, or an insulator.[25]

Since both the core diamagnetism and the Van Vleck paramagnetism are essentially temperature independent, the observed temperature dependence of the measured magnetic susceptibility and its variation with the hole content must result from the spin susceptibility $\chi_{\rm spin}(T)$. Two alternate physical descriptions of the origin of $\chi_{\rm spin}(T)$ have been proposed. The starting point for the first model (model I) is the fact that the undoped systems La_2CuO_4 and $YBa_2Cu_3O_6$ can be characterized as quasi-two-dimensional Heisenberg antiferromagnets on a square lattice, with the $S=\frac{1}{2}$ spins located on the Cu sites. The three-dimensional (3D) ordering in these systems is due to the coupling between the (sets of) two-dimensional CuO_2 planes. This results in an effective interplane exchange energy $\mathcal{J}_\perp$ which is several orders of magnitude smaller than the intraplane Cu-Cu superexchange energy $\mathcal{J}$.[27,28] Introducing holes drastically reduces the interplane exchange energy, the in-plane exchange energy, the in-plane magnetic correlation length, as well as the magnetic moments on the Cu sites.[7,29] Ultimately the 3D magnetic order is lost and the metallic state is reached, but the in-plane magnetic correlation length remains finite.[29] The experimental observation[30] that the doped holes are primarily on the oxygen sites led to the proposal that the doped holes form one band and interact only slightly with the spin background of the local Cu^{2+} spins, which forms a second band.[31] If this is correct, it should be possible to decompose the spin susceptibility into two independent parts, an effective temperature-independent Pauli paramagnetism from the band of doped holes and a temperature-dependent susceptibility originating from the residual two-dimensional antiferromagnetic correlations on the planar Cu sublattice. In model I, therefore, the spin susceptibility can be written $\chi_{\rm spin}(T)=\chi_{\rm Pauli}+\chi_{\rm 2D}(T)$.[6] This model accounts in a natural way for the broad susceptibility maximum of $La_{2-x}Sr_xCuO_4$ which shifts with increasing hole content to lower temperatures.[2,3,6] Interestingly, the blowup of the measured susceptibility data for $Bi_2Sr_2CaCuO_{8.11}$ in Fig. 4 reveals a broad susceptibility maximum which apparently shifts with higher oxygen content (hole content) to lower temperatures [see Fig. 2(b)]. This behavior is observed particularly clearly in recent data on the single-layer $Bi_2Sr_{2-x}La_xCuO_{6+y}$ compound as a function of the lanthanum and oxygen content.[15,32]

The temperature dependence of the magnetic susceptibility of a 2D Heisenberg antiferromagnet on a square lattice was first calculated by Lines[33] using the method of high-temperature series expansion:

$$\chi_{\rm 2D}(T)=2N_0g^2\mu_B^2\frac{1}{\mathcal{J}}\left[3\Phi+\sum_{n=1}^{\infty}\frac{C_n}{\Phi^{n-1}}\right]^{-1}, \quad (2)$$

where $\Phi=k_B[T/2\mathcal{J}S(S+1)]$. Here, N_0 is the number of spins per mole and g the Landé g factor. C_n are coefficients tabulated by Lines.[33] This susceptibility contribution $\chi_{\rm 2D}(T)$ shows a broad maximum at a temperature $T_{\rm max}$ which is a function of S and the in-plane exchange constant $\mathcal{J}$. De Jongh[34] extended the calculations and derived an expression for the temperature at the susceptibility maximum

$$T_{\rm max}=2.53S(S+1)\mathcal{J}(K)/k_B\ , \quad (3)$$

where the susceptibility takes on the value

$$\chi_{\rm 2D}(T_{\rm max})=\frac{N_0\mu_{\rm eff}^2}{S(S+1)}\frac{1}{\mathcal{J}}\ , \quad (4)$$

where $\mu_{\rm eff}$ is the effective moment. To date no theory exists which describes how the susceptibility of a two-dimensional antiferromagnet is altered as charge carriers are introduced. Therefore, using Eq. (3) with $S=\frac{1}{2}$ and the temperature of the susceptibility maximum for $Bi_2Sr_2CaCuO_{8.11}$ ($T_{\rm max}\simeq 360$ K) yields a value of $\mathcal{J}/k_B\simeq 190$ K. With this value, assuming $g=2$ for the copper ions (common values for copper ions are $g=2.1$–2.4), and that $\mu_{\rm eff}^2=g^2S(S+1)\mu_B^2$, a value of $\chi_{\rm 2D}(T_{\rm max})=+7.9\times10^{-4}$ cm^3/mol is obtained from Eq. (4). This value lies well above the experimental value (see Fig. 2). This reduction in the experimental value of the susceptibility may originate from a weakening of the effective moment $\mu_{\rm eff}$ of the copper ions, in qualitative agreement with the observations of neutron-scattering experiments for $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$.[7] It would thus seem reasonable to analyze the experimental data in Fig. 2(b) on $Bi_2Sr_2CaCuO_{8+y}$ using the expression

$$\chi(T)=\chi_0+\chi_{\rm 2D}(T)\ , \quad (5)$$

where χ_0, $\mu_{\rm eff}$, and $\mathcal{J}$ are treated as fit parameters. An analysis on this basis was first undertaken by Johnston[6] for susceptibility measurements on $La_{2-x}Sr_xCuO_4$. The result of the fit to the susceptibility data on $Bi_2Sr_2CaCuO_{8.11}$ with Eq. (5) for $\chi_0=+0.83\times10^{-4}$ cm^3/mol, $\mu_{\rm eff}=0.82\mu_B$, and $\mathcal{J}/k_B=194$ K is shown in Fig. 4. The resulting fit parameters for all oxygen concentrations studied are given in Table II. The standard deviation is for all fits better than 0.5% of the measured values. χ_0 is a temperature-independent constant and

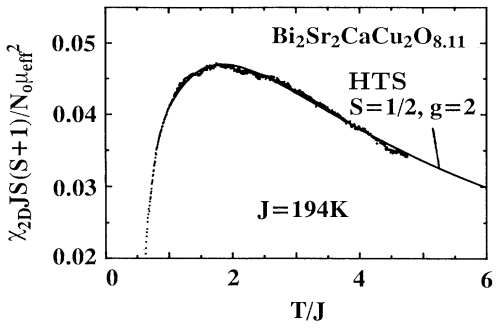

FIG. 4. Measured normalized susceptibility after subtraction of χ_0 versus the normalized temperature. The solid line gives the fit of the data with the theoretical curve of a two-dimensional Heisenberg antiferromagnet on a square lattice with $S=\frac{1}{2}$ and $g=2$. The fit parameters are $\mathcal{J}/k_B=194$ K and $\mu_{\rm eff}=0.83\mu_B$. The fit is shown only for values of $k_BT/\mathcal{J}$ greater than 1. Note that in this figure $J\equiv\mathcal{J}/k$.

TABLE II. The results of the fits to the susceptibility of $Bi_2Sr_2CaCu_2O_{8+y}$. Given are the three fit parameters χ_0, $\mathcal{J}$, and μ_{eff} together with values of both the Pauli susceptibility and T_c from the Meissner transition. The asterisks indicate units of 10^{-4} cm^3/mol.

y	0.11	0.16	0.19	0.22	0.24
T_c (K)	86.5	92.8	87.1	77.6	71.1
$\mathcal{J}/k_B$ (K)	194	85.6	48.9	39.3	21.2
μ_{eff} (μ_B)	0.834	0.709	0.682	0.702	0.616
χ_0*	0.86	1.07	1.17	1.25	1.49
χ_{Pauli}*	2.06	2.27	2.37	2.45	2.69

represents the sum of the core diamagnetism, the Van Vleck paramagnetism, and the Pauli paramagnetism

$$\chi_0=\chi_{\text{core}}+\chi_{\text{VV}}+\chi_{\text{Pauli}} . \quad (6)$$

From the above data on χ_{core} and χ_{VV}, the Pauli susceptibility χ_{Pauli} can thus be estimated from the fit data, as given in Table II. We note that $Bi_2Sr_2CaCuO_{8.16}$ shows nearly the same reduction in the magnitude of the susceptibility maximum $\chi_{2D}(T_{\max})$, to only 4% of that expected for $g\simeq 2$, as does $La_{1.8}Sr_{0.2}CuO_4$.[6] In both cases this would correspond to a reduction by a factor of 5 in the effective magnetic moment per copper ion. Clearly the reliability of the fits for $y\geq 0.19$ will be less satisfactory because in these cases the $\chi(T)$ data lack structure; indeed, the calculated position of the susceptibility maximum ($T_{\max}\simeq 1.9\mathcal{J}/k_B$) is below the superconducting transition temperature T_c so that the normal-state susceptibility would be expected to simply decrease monotonically with increasing temperature. Another source of error arises from the structural disorder introduced as the oxygen content is increased from $y=0.11$ to 0.24. This disorder may lead to an enhanced Curie-like behavior for those samples with higher oxygen content, thus causing a significant falsification of the values of the parameters given in Table II, especially for the magnetic exchange constant $\mathcal{J}$.

In contrast to the double-layer bismuth system, the magnetic susceptibility of single-layer $Tl_2Ba_2CuO_{6+y}$ [see Fig. 2(a)] can be quite well described by a Curie-Weiss law plus a constant; no maximum is seen for any oxygen concentration. However, a close inspection of the data reveals that for temperatures above 400 K the slope $d\chi/dT$ changes from positive to negative as the oxygen content is increased. It is certainly possible that the large Curie-Weiss tail at low temperature masks the broad susceptibility maximum. This Curie-Weiss tail is presumably caused by disorder effects of surplus interstitial oxygen which appear to play a crucial role in the single-layer thallium system, as indicated by high-pressure experiments and neutron-scattering experiments.[35,36]

The temperature dependence of the susceptibility of $YBa_2Cu_3O_{6+y}$ (Ref. 9) does not appear to exhibit a distinct maximum, although at low oxygen content a maximum might exist at temperatures above 1000 K;[7,9] the susceptibility flattens out with increasing hole content, without any observable shift of a maximum. Due to structural instabilities, it is not possible to reach far into the high-hole side of the $T_c(P)$ phase diagram of $YBa_2Cu_3O_{6+y}$ by increasing the oxygen content beyond $y=1$. Perhaps in $YBa_2Cu_3O_{6+y}$ the magnetic moment on the copper site is for some reason much more rapidly suppressed with increasing hole content than in $Bi_2Sr_2CaCuO_{8+y}$ and $La_{2-x}Sr_xCuO_4$. This could lead to the observed flattening as the oxygen content is raised to $y=1$. In this context an experiment in which the hole content of $YBa_2Cu_3O_{6+y}$ is changed in a controlled manner from the low-hole side of the T_c maximum to the high-hole side would be highly desirable. The agreement between the present model I and the experimental data is clearly not entirely satisfactory. In the following we discuss an alternate model.

In the above model I the doped holes in the oxygen sites form a conduction band which is distinct and only weakly interacting with the spin background of the local Cu^{2+} spins which form a second band. It has been proposed,[37] however, that the doped holes interact strongly with the copper spins so that together they form a strongly correlated spin system in a single band, i.e., like spin singlets in the t-$\mathcal{J}$ model. In this proposal, which we will call model II, the spin susceptibility consists of only a single component which itself is regarded as the temperature-dependent Pauli susceptibility, i.e., $\chi_{\text{spin}}(T)=\chi_{\text{Pauli}}(T)$. NMR results,[38,39] together with the success of the phenomenological "antiferromagnetic Fermi-liquid theory"[40,41] in explaining the measured NMR data, point to this possibility. However, model II is not yet able to account for the negative slopes of the susceptibility for those samples situated on the high-hole side of the $T_c(P)$ phase diagram, like the specimens with $y\geq 0.16$ in Fig. 2. The negative susceptibility slopes observed may arise from additional Curie-Weiss-like behavior from free paramagnetic moments introduced by the increase in oxygen content. As was already speculated for $La_{2-x}M_xCuO_4$ (M=Sr,Ba) on the high-hole side,[42] such free moments may act as pair-breaking centers which would drive T_c down more the higher the Curie constant. Unfortunately, it is not possible to analyze the present data in terms of pair-breaking theory.

In the following we will analyze the susceptibility data at that hole concentration p for which T_c takes on its maximum value. The reason for this choice is that, for this optimal value of p, the susceptibility $\chi(T)$ is almost independent of temperature (for all compounds studied the maximal variation is less than 10% of $\chi-\chi_{\text{core}}$), thus simplifying the analysis. To proceed with the analysis of our data, we apply the single-band model II where $\chi_{\text{Pauli}}=\chi_{\text{spin}}$. As we point out below, using model I to analyze the data only leads to a minimal reduction ($\sim$20%) in the estimated value of $N(E_F)$. Using the room-temperature values of the susceptibility $\chi^+(300\text{ K})$ from Fig. 3, which have already been corrected for the core diamagnetism, we obtain

$$\chi_{\text{Pauli}}=\chi^+(300\text{ K})-\chi_{\text{VV}} . \quad (7)$$

We neglect here the Landau diamagnetism of the charge carriers which is given by the expression $\chi_L=-\frac{1}{3}\chi_{\text{Pauli}}(m/m^*)^2$. Since $m^*/m\approx 3$–4,[43,44] χ_L

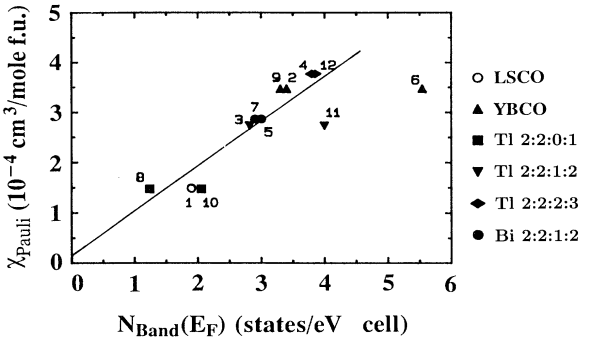

FIG. 5. Measured Pauli susceptibility versus the bare density of states at the Fermi energy from band-structure calculations. The abbreviations have the same meanings as in Figs. 1 and 3 . The references are (1) Yu *et al.* (Ref. 45), (2) Massidda *et al.* (Ref. 46), (3) and (4) Yu *et al.* (Ref. 47), (5) Massidda *et al.* (Ref. 48), (6) and (7) Krakauer *et al.* (Refs. 49 and 50), (8) Hamann *et al.* (Ref. 51), (9) Herman *et al.* (Ref. 52), (10)–(12) Kasowski *et al.* (Ref. 53). The data for $La_{1.85}Sr_{0.15}CuO_{4+y}$ are taken from Ref. 2.

should be more than an order of magnitude smaller than the Pauli paramagnetism. Table I shows the results of the estimated values of χ_{Pauli} for the different compounds. In Fig. 5, we plot the χ_{Pauli} data from Table II versus the bare densities of states at the Fermi energy $N_{band}(E_F)$ from band-structure calculations. In this comparison we assume that the results of the band-structure calculations, which do not account for disorder or effects of nonstoichiometry, are valid for the samples with optimal T_c. In spite of this rough approximation, a linear correlation between the Pauli susceptibility and the density of states at the Fermi level $N_{band}(E_F)$ is evident in Fig. 5. This result is consistent with the behavior expected for Fermi liquids given by the expression

$$\chi_{Pauli} = A\mu_B N_{band}(E_F) , \quad (8)$$

where A is the enhancement factor. From the slope of the straight line in Fig. 5, we obtain the sizable value $A = 2.8$. If this linear correlation between the Pauli susceptibility and the calculated density of states is not accidental, band-structure calculations appear to give reliable results for those high-T_c materials with optimal T_c, although they fail to predict the properties of oxides with low carrier concentrations where the magnetic correlations are strong. On the other hand, even for samples with the highest values of T_c it would appear that residual antiferromagnetic correlations still exist, leading to an enhancement of the spin susceptibility.

These conclusions are not altered in any significant way if model I is used to analyze the present data. Analysis with model I results in estimates of the Pauli susceptibility which are somewhat ($\sim$20%) less, as is seen by comparing the respective values for $Bi_2Sr_2CaCu_2O_{8.16}$ in Tables I and II. Thus, using model I only results in a reduction in the estimate of A of approximately 20%, but leaves the main result, the linear dependence of χ_{Pauli} and $N_{band}(E_F)$, unchanged.

V. CONCLUSIONS

The measurement of the static magnetic susceptibility of a variety of high-temperature superconductors indicates a correlation between the temperature derivative $d\chi/dT$ of the magnetic susceptibility in the normal state and the transition temperature T_c. We conclude that the magnetic susceptibility in the normal state is mainly determined by the CuO_2 layers. The linear relationship between the estimated Pauli paramagnetism for those systems with optimal T_c values and the calculated band-structure density of states at the Fermi energy is consistent with models which treat the superconducting oxides like correlated Fermi liquids.

The results of this work allow us to suggest an empirical procedure for reaching the highest possible value of T_c within a given compound system: first, measure the room-temperature susceptibility of the system and correct for core diamagnetism. If the resulting value at 300 K is larger than $\chi^+ \approx +n(1.9\times10^{-4}$ cm^3/mol f.u.), where n is the number of CuO_2 layers per formular unit, then lower the oxygen (hole) content of the specimen. If the measured susceptibility is less than this value, then increase the oxygen (hole) content of the sample. When the optimal value of T_c has been reached, the magnetic susceptibility in the normal state should be nearly temperature independent for temperatures above $2T_c$.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to W. Reith (University of Munich) and J. Bock (Hoechst AG) for providing the excellent samples. Special thanks are due to J. J. Neumeier for helpful discussions and for critically reading the manuscript. This work was supported by the Deutsche Forschungsgemeinschaft and the Bundesministerium für Forschung und Technologie.

*Present address: Osram GmbH, FL/N-M, Hellabrunnerstr. 1, W-8000 München 90, Germany.

[1]James S. Schilling and Stefan Kotz, in *Physical Properties of High Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Singapore, 1992), Vol. III, p. 59.

[2]J. B. Torrance, A. Bezinge, A. I. Nazzal, T. C. Huang, S. S. Parkin, D. T. Keane, S. J. LaPlaca, P. M. Horn, and G. A. Held, Phys. Rev. B **40**, 8872 (1989).

[3]H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, and Y. Tokura, Phys. Rev. B **40**, 2254 (1989).

[4]W. A. Groen, D. M. de Leeuw, and L. F. Feiner, Physica C **165**, 55 (1990).

[5]B. Batlogg, in *High Temperature Superconductivity: The Los Alamos Symposium,* edited by K. Bedell, D. Coffey, D. Meltzer, D. Pines, and J. R. Schrieffer (Addison-Wesley, Reading, MA, 1990).

[6]D. C. Johnston, Phys. Rev. Lett. **62**, 957 (1989).
[7]J. M. Tranquada, A. H. Mouden, A. I. Goldmann, P. Zolliker, D. E. Cox, G. Shirane, S. K. Sinha, D. Vaknin, D. C. Johnston, M. S. Alvarez, A. J. Jacobson, J. T. Lewandowski, and J. M. Newsam, Phys. Rev. B **38**, 2477 (1988).
[8]Y. Nakazawa and M. Ishikawa, Physica C **158**, 381 (1989).
[9]C. Allgeier, R. Sieburger, H. Goßner, J. Diederichs, H. Neumaier, W. Reith, P. Müller, and J. S. Schilling, Physica C **162**, 741 (1989).
[10]W. Reith, P. Müller, C. Allgeier, R. Hoben, J. Heise, J. S. Schilling, and K. Andres, Physica C **156**, 319 (1988).
[11]C. Allgeier, J. J. Neumeier, and J. S. Schilling, Physica C **194**, 337 (1992).
[12]C. Allgeier, J. Heise, W. Reith, J. S. Schilling, and K. Andres, Physica C **157**, 293 (1989).
[13]W. Reith, C. Allgeier, K. Andres, J. Heise, R. Hoben, A.-K. Klehe, R. Kleiner, C. Kowal, A. Moise, P. Müller, and J. S. Schilling, Physica C **162**, 109 (1989).
[14]C. Allgeier and J. S. Schilling, Physica C **168**, 499 (1990).
[15]A. Schlögl, J. J. Neumeier, J. Diederichs, C. Allgeier, J. S. Schilling, W. Yelon, and R. Sieburger, Physica C (to be published).
[16]B. Batlogg, in *Physical Proproperties of High-Temperature Superconductors,* edited by S. Maekawa and M. Sato, Springer Series in Solid-State Sciences Vol. 106 (Springer, Berlin, 1992), p. 219.
[17]R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Rietman, Phys. Rev. B **35**, 5337 (1987).
[18]W. C. Lee, R. A. Klemm, and D. C. Johnston, Phys. Rev. Lett. **63**, 1012 (1989).
[19]*Landolt-Börnstein, New Series,* Group II, Vol. 16, edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Heidelberg, 1986), p. 402.
[20]From the data fits we find $\chi_{\text{Curie-Weiss}}=0.0437/(T-8.4\ \text{K})$ $\text{cm}^3\,\text{K/mol}$ and $0.123/(T-24.6\ \text{K})$ $\text{cm}^3\,\text{K/mol}$ for Tl 2:2:1:2 and Tl 2:2:2:3, respectively.
[21]A. Hofmann, H. Kronmüller, N. Moser, R. Reisser, P. Schüle, and F. Dworschak, Physica C **156**, 528 (1988).
[22]M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, J. L. Smith, and R. B. Schwarz, Phys. Rev. B **39**, 300 (1989); M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, K. C. Ott, and J. D. Thompson, Phys. Rev. Lett. **63**, 1865 (1989).
[23]U. Bremer, Diplom thesis, Sektion Physik der Universität München, 1990.
[24]H. P. Geserich, B. Koch, G. Schreiber, J. Geerk, H. C. Li, G. Linker, W. Weber, and W. Assmus, Physica C **153-155**, 661 (1988).
[25]W. C. Lee and D. C. Johnston, Phys. Rev. B **41**, 1904 (1990).
[26]A. Trokiner, R. Mellet, A.-M. Pougnet, D. Morin, Y. M. Gao, J. Primot, and J. Schneck, Phys. Rev. B **41**, 9570 (1990).
[27]L. J. de Jongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974).
[28]J. Rossat-Mignod, L. P. Regnault, M. J. Jurgens, C. Vettier, P. Burlet, J. Y. Henry, and G. Lapertot, Physica C **162-164**, 1269 (1989).
[29]R. J. Birgeneau, Y. Endoh, Y. Hidaka, K. Kakurai, M. A. Kastner, T. Murakami, G. Shirane, T. R. Thurston, and K. Yamada, IBM J. Res. Dev. **33**, 270 (1989).
[30]J. Fink, N. Nücker, H. A. Romberg, and J. C. Fuggle, IBM J. Res. Dev. **33**, 372 (1989).
[31]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).
[32]A. Schlögl, Diplom thesis, University of Munich, 1992.
[33]M. E. Lines, J. Phys. Chem. Solids **31**, 101 (1970).
[34]L. J. de Jongh, in *Magnetism and Magnetic Materials 1972, (Denver),* Proceedings of the 18th Annual Conference on Magnetism and Magnetic Materials, AIP Conf. Proc. No. 10, edited by C. D. Graham and J. Rhyne (AIP, New York, 1972), p. 561.
[35]R. Sieburger and J. S. Schilling, Physica C **173**, 403 (1991).
[36]H. Takahashi, J. D. Jorgensen, B. A. Hunter, R. L. Hitterman, S. Pei, F. Izumi, Y. Shimakawa, Y. Kubo, and T. Manako, Physica C **191**, 248 (1992).
[37]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 9423 (1988).
[38]H. Alloul, T. Ohno, and P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989).
[39]R. E. Walstedt and W. W. Warren, Science **248**, 1082 (1990).
[40]A. J. Millis, H. Monien, and D. Pines, Phys. Rev. B **42**, 167 (1990).
[41]H. Monien, D. Pines, and M. Takigawa, Phys. Rev. B **43**, 258 (1991); H. Monien, P. Monthoux, and D. Pines, *ibid.* **43**, 275 (1991).
[42]M. Oda, T. Nakano, Y. Kamada, and M. Ido, Physica C **183**, 234 (1991).
[43]K. Kitazawa, IBM J. Res. Dev. **33**, 201 (1989).
[44]J. L. Smith, C. M. Fowler, B. L. Freeman, W. L. Hults, J. C. King, and R. M. Mueller, *Proceedings of the 3rd International Symposium on Superconductivity,* Sendai, Japan, 1990 (Springer-Verlag, Berlin, 1990).
[45]J. Yu, A. J. Freeman, and J. H. Xu, Phys. Rev. Lett. **58**, 1035 (1987).
[46]S. Massidda, J. Yu, and A. J. Freeman, Phys. Lett. A **122**, 198 (1987).
[47]J. Yu, S. Massidda, and A. J. Freeman, Physica C **152**, 273 (1988).
[48]S. Massidda, J. Yu, and A. J. Freeman, Physica C **152**, 251 (1988).
[49]H. Krakauer, W. E. Pickett, and R. E. Cohen, J. Supercond. **1**, 111 (1988).
[50]H. Krakauer and W. E. Pickett, Phys. Rev. Lett. **60**, 1665 (1988).
[51]D. R. Hamann and L. F. Mattheiss, Phys. Rev. B **38**, 5138 (1988).
[52]F. Herman, R. V. Kasowski, and W. Y. Hsu, Phys. Rev. B **36**, 6904 (1987).
[53]R. V. Kasowski, W. Y. Hsu, and F. Herman, Phys. Rev. B **38**, 6470 (1988).