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# $^{17}O$ nuclear-magnetic-resonance spin-lattice relaxation and Knight-shift behavior in bismuthate, plumbate, and cuprate superconductors

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We have measured the $^{17}O$ nuclear-magnetic-resonance spin-lattice relaxation times ($T_1$) as a function of temperature for the $CuO_2$ planar sites in $Tl_2Ba_2CaCu_2O_{8+x}$, $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2CaCu_2O_{8+x}$, $La_{1.85}Sr_{0.15}CuO_{4-x}$, $La_{1.85}Ca_{0.15}CuO_{4-x}$, and $Bi_2Sr_2CuO_{6+x}$, as well as for the oxygen sites in $Ba_{0.6}K_{0.4}BiO_3$, $BaBi_{0.25}Pb_{0.75}O_3$, $BaSb_{0.25}Pb_{0.75}O_3$, and $BaPbO_3$. The $CuO_2$ planar sites in $Tl_2Ba_2CaCu_2O_{8+x}$, $YBa_2Cu_3O_{7-x}$, and $Bi_2Sr_2CaCu_2O_{8+x}$ exhibit close to ideal Korringa behavior in the normal state, characteristic of a good metal. In addition, the Knight shift of the $CuO_2$ planes in these three materials is dominated by a spin contribution that is temperature independent in the normal state and vanishes in the superconducting state. The relaxation times of the BaO and SrO planar oxygens, as well as of the TlO planar oxygens, are much longer than those of the $CuO_2$ planes, and are similar to the values found for the bismuthate and plumbate materials. In both lanthanum cuprates, the frequency shift of the $CuO_2$ plane is temperature dependent in the normal state. Relaxation-rate data, when plotted as a function of $\ln(T_c)$, show a clear difference between the bismuthate (plumbate) and cuprate materials, and appear consistent with BCS-like behavior for the copper-free systems.

A large number of nuclear-magnetic-resonance (NMR) studies have recently been carried out on the high-$T_c$ copper oxide superconductors, and have yielded considerable insight into their unusual magnetic and electronic properties, in both the normal and superconducting states. For example, information concerning the dynamic and static spin susceptibilities, density of states, and the presence of antiferromagnetic spin fluctuations has been obtained through $^{65,63}Cu$, (Refs. 1-4), $^{89}Y$, (Refs. 5-7), and $^{17}O$ (Refs. 8-12) NMR studies of $YBa_2Cu_3O_{7-x}$. Comparative studies with other systems, including copper-free materials, should, in our view, be useful for discerning which properties, as observed by NMR, are directly related to the pairing mechanism. In this paper we report the results of such a comparative study of the $^{17}O$ NMR relaxation and spin-susceptibility behavior of the cuprate superconductors: $Tl_2Ba_2CaCu_2O_{8+x}$ ($T_c=95$ K), $YBa_2Cu_3O_{7-x}$ ($T_c=92$ K), $Bi_2Sr_2CaCu_2O_{8+x}$ ($T_c=74$ K), $La_{1.85}Sr_{0.15}CuO_{4-x}$ ($T_c=38$ K), $La_{1.85}Ca_{0.15}CuO_{4-x}$ ($T_c=22$ K), and $Bi_2Sr_2CuO_{6+x}$ ($T_c=5.6$ K), as well as with the bismuthate and plumbate materials: $Ba_{0.6}K_{0.4}BiO_3$ ($T_c=28$ K), $BaBi_{0.25}Pb_{0.75}O_3$ ($T_c=10$ K), $BaSb_{0.25}Pb_{0.75}O_3$ ($T_c=2.6$ K), and $BaPbO_3$. Our results indicate that while the relaxation behavior of the noncopper containing oxide superconductors is consistent with a BCS-like relationship between the electronic density of states and $T_c$:$(T_1T)^{1/2}\alpha \ln T_c$, $T_1T$ values for the $CuO_2$ planes of the cuprates do not vary appreciably with their critical temperatures.

$^{17}O$-labeled samples were synthesized from oxide or oxide carbonate mixtures as described previously,[9] and annealed in a circulating or static 35–50% $^{17}O_2$ (Monsanto Research Corporation, Miamisburg, OH) atmosphere.[13] One $BaSb_{0.25}Pb_{0.75}O_3$ sample was provided by Cava at AT&T Bell Laboratories, and was reannealed in a circulating $^{17}O_2$ atmosphere at 830 °C for 5 h. This sample's x-ray diffraction pattern, NMR spectrum, and relaxation data were identical to another $BaSb_{0.25}Pb_{0.75}O_3$ sample prepared in this laboratory. The $Ba_{0.6}K_{0.4}BiO_3$ sample was prepared and enriched by Hinks at Argonne National Laboratory. Powder x-ray analysis of all the $^{17}O$-enriched samples showed them to be essentially single phase and in accord with literature diffraction patterns.[14] The $T_c$ onsets, given above, were measured with a S.H.E. (San Diego, CA) or Quantum Design (San Diego, CA) superconducting quantum interference magnetometer, and were all close to the expected values. $^{17}O$ NMR spectra and relaxation rates were measured at 8.45 or 11.7 T using a spin-echo technique.[15] Low-temperature measurements were carried out at 8.45 T with a continuous flow cryostat (Oxford Instruments, Osney Mead, U.K.) Model CF1200. The $^{17}O$ frequency shifts are reported relative to an external standard of tap water. The chemical shift of oxygen in water, relative to that of the bare oxygen nucleus, has been calculated to be less than 0.04% (400 ppm).[16] We have found that the chemical shifts of most diamagnetic oxides will be in the range −200 to +700 ppm from $H_2O$ (where high-frequency, low-field, paramagnetic, or deshielded values are positive [International Union of Pure and Applied Chemistry (IUPAC)] δ scale).[9]

We show in Fig. 1 the $^{17}$O NMR spectra of most of the compounds studied. All the cuprates contain a highly paramagnetically shifted resonance, assigned to oxygens in the $CuO_2$ planes, and resonance(s) in a diamagnetic region, assigned to the other oxygen sites. The $La_{1.85}Ca_{0.15}CuO_{4-x}$ spectrum, not shown, is nearly identical to that of $La_{1.85}Sr_{0.15}CuO_{4-x}$. For all the bismuthates (plumbates), field-dependent measurements are consistent with line shapes dominated by the electric quadrupolar interaction. Using "magic-angle" sample spinning, we obtain well resolved spectra for $BaBiO_3$ and $BaPbO_3$ consistent with quadrupole coupling constants of 6.5 and 7.7 MHz asymmetry parameter ($\eta=0$), and isotropic chemical shifts of 350 and 330 ppm. Similar spinning spectra of the doped samples are not as well resolved, suggesting the increased importance of anisotropic chemical/Knight-shift interactions (or a heterogeneous distribution of shifts and/or coupling constants).

We show in Figs. 2(a)–2(d) the temperature dependence of the relaxation rates and frequency shifts of $Tl_2Ba_2CaCu_2O_{8+x}$, $YBa_2Cu_3O_{7-x}$ $Bi_2Sr_2CaCu_2O_{8+x}$, $La_{1.85}Sr_{0.15}CuO_{4-x}$, $La_{1.85}Ca_{0.15}CuO_{4-x}$, $Bi_2Sr_2CuO_{6+x}$, $Ba_{0.6}K_{0.4}BiO_3$, $BaBi_{0.25}Pb_{0.75}O_3$, $BaSb_{0.25}Pb_{0.75}O_3$, and $BaPbO_3$. For $YBa_2Cu_3O_{7-x}$, $La_{1.85}Sr_{0.15}CuO_{4-x}$, and $La_{1.85}Ca_{0.15}CuO_{4-x}$, the measurements were performed on magnetically oriented crystallites, while for the other samples, randomly oriented powders were used. For the copper-free oxides, the relaxation measurements were carried out on the high-frequency edge of the powder line shapes in an effort to minimize contributions from any possibly undoped sample regions. The nuclear spin-lattice relaxation times were measured on the central transitions using an inversion-recovery pulse sequence, and fit to the appropriate triple exponential recovery curves for a spin $I=\frac{5}{2}$ nucleus.[17]

As can be seen from Figs. 2(a) and 2(c), the relaxation rates of the $CuO_2$ planar oxygens in the higher-$T_c$ copper oxide materials, as well as the oxygen sites in the other metal oxide superconductors, all exhibit Korringa-like behavior in the normal state. The Korringa relation

$$K_S^2 T_1 T = S, \quad S = \frac{\hbar}{4\pi k_B}\left[\frac{\gamma_e}{\gamma_n}\right]^2 \qquad (1)$$

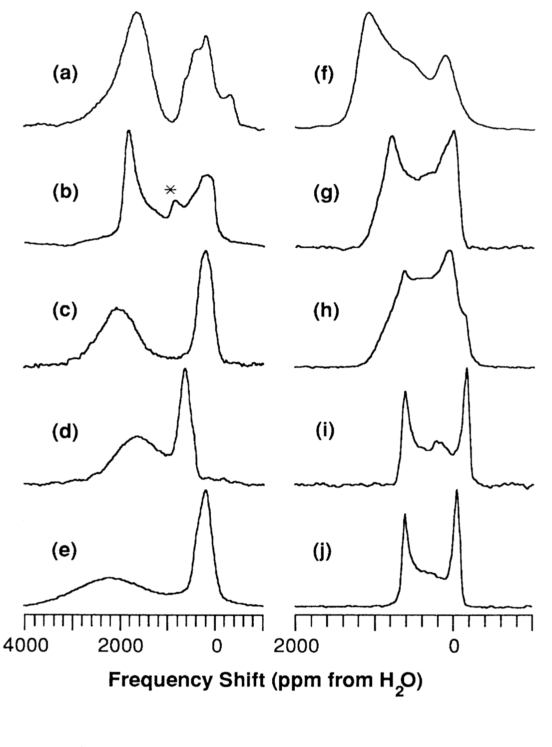

FIG. 1. $^{17}$O NMR spectra at 300 K and 8.45 T (48.8 MHz) of (a) $Tl_2Ba_2CaCu_2O_{8+x}$, (b) $YBa_2Cu_3O_{7-x}$, (c) $Bi_2Sr_2CaCu_2O_{8-x}$, (d) $La_{1.85}Sr_{0.15}CuO_{4-x}$, (e) $Bi_2Sr_2CuO_{6+x}$ (f) $Ba_{0.6}K_{0.4}BiO_3$, (g) $BaBi_{0.25}Pb_{0.75}O_3$, (h) $BaSb_{0.25}Pb_{0.75}O_3$, (i) $BaPbO_3$, and (j) $BaBiO_3$. The $*$ in (b) represents O(1) sites in a small population of aligned crystallites. All spectra were acquired using random powder samples, except for (d) $La_{1.85}Sr_{0.15}CuO_{4-x}$, which is from a sample of magnetically aligned crystallites in epoxy.

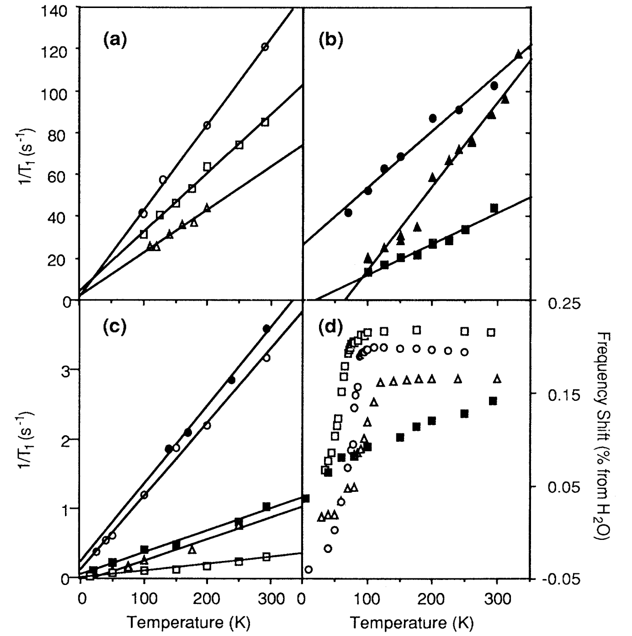

FIG. 2. $^{17}$O NMR spin-lattice relaxation rate and frequency shifts for oxide superconductors, as a function of temperature, at 8.45 T. (a) Relaxation rates of the $CuO_2$ plane oxygen sites of ○, $YBa_2Cu_3O_{7-x}$; □, $Bi_2Sr_2CaCu_2O_{8+x}$; △, $Tl_2Ba_2CaCu_2O_{8+x}$. (b) Relaxation rates of the $CuO_2$ plane oxygen sites of ▲, $La_{1.85}Sr_{0.15}CuO_{4-x}$; ■, $La_{1.85}Ca_{0.15}CuO_{4-x}$; and ●, $Bi_2Sr_2CuO_{6+x}$. (c) Relaxation rates of ○, $Ba_{0.6}K_{0.4}BiO_3$; ●, $Ba_{0.6}K_{0.4}BiO_3$ (at 11.7 T); ■, $BaBi_{0.25}Pb_{0.75}O_3$; △, $BaSb_{0.25}Pb_{0.75}O_3$; □, $BaPbO_3$. (d) Frequency shifts of the $CuO_2$ plane oxygen sites of ○, $YBa_2Cu_3O_{7-x}$; □, $Bi_2Sr_2CaCu_2O_{8+x}$; △, $Tl_2Ba_2CaCu_2O_{8+x}$; ■, $La_{1.85}Ca_{0.15}CuO_{4-x}$.

is valid if the electronic states at the Fermi surface have significant $s$ character. $K_S$ is the spin part of the total measured Knight shift, which also contains an orbital contribution, $K_{\mathrm{orb}}$. The Korringa ratio, $K_S^2 T_1 T/S$, gives an estimate of the deviation from ideal behavior. Even in the simple $s$-electron metals, deviations from an ideal Korringa ratio of unity can arise from electron-electron interactions.[18]

We show in Fig. 2(d) the temperature dependence of the frequency shifts of the $\mathrm{CuO_2}$ planar oxygens for the three higher-$T_c$ copper oxide superconductors and $\mathrm{La_{1.85}Ca_{0.15}CuO_{4-x}}$. For $\mathrm{YBa_2Cu_3O_{7-x}}$ and $\mathrm{La_{1.85}Ca_{0.15}CuO_{4-x}}$ the $\mathrm{CuO_2}$ planar oxygen frequency shift component for the crystalline $c$ axis aligned with the applied field is shown, while for $\mathrm{Bi_2Sr_2CaCu_2O_{8+x}}$ and $\mathrm{Tl_2Ba_2CaCu_2O_{8+x}}$ the frequency shifts were measured from the random powder line shapes. Our frequency shift measurements of $\mathrm{YBa_2Cu_3O_{7-x}}$ are consistent with those of Takigawa *et al.*[19] In the normal state, for the higher-$T_c$ cuprates, the spin Knight shifts of the $\mathrm{CuO_2}$ planar oxygens are temperature independent, and then vanish as the materials become fully superconducting, leaving a small orbital contribution. $K_{\mathrm{orb}}$ cannot be measured by simply extrapolating our frequency shifts to $T=0$ K, since demagnetization corrections are necessary. Barrett *et al.*[4] applied such a correction to the Cu shifts of $\mathrm{YBa_2Cu_3O_{7-x}}$ by using the $^{89}$Y resonance frequency as a measure of the internal field, $B_{\mathrm{int}}$. They found that at 4.2 K, $B_{\mathrm{int}}$ is 0.05% lower than $H_0$ when $\mathbf{H}\|c$. Applying such a correction to the extrapolated value of $K\sim-0.04$ at $T=0$ K for O(2,3), an estimate of $K_{\mathrm{orb}}\sim0.01\%$ is found. However, this correction is not exact since the measured value of $B_{\mathrm{int}}$ is sample dependent. The frequency shifts of the diamagnetic $\mathrm{CuO_2}$ precursor materials[9] give another estimate of $K_{\mathrm{orb}}\sim-0.01\%$. Averaging these values yields a conservative error estimate for $K_{\mathrm{orb}}\sim0.0\pm0.02\%$. Using the slope of $1/T_1$ versus $T$, and the isotropic Knight shift, $K_{\mathrm{iso}}=0.223\%$,[9] we obtain a Korringa ratio of $K_S^2 T_1 T/S\sim0.8\pm0.2$ for $\mathrm{YBa_2Cu_3O_{7-x}}$, in agreement with the result of 0.7 of Hammel *et al.*[10] Assuming similar $K_{\mathrm{orb}}$ values and small Knight-shift anisotropies, the Korringa ratios for the thallium and bismuth copper oxide materials are $0.8\pm0.2$ and $1.0\pm0.2$, respectively. Even with the error for $K_{\mathrm{orb}}$ included, the Korringa ratios in the higher-$T_c$ materials are all close to unity, which is characteristic of simple metals with minimal electron-electron correlation effects.

The normal-state frequency shifts of the $\mathrm{CuO_2}$ planar site of $\mathrm{La_{1.85}Sr_{0.15}CuO_{4-x}}$, not shown, and $\mathrm{La_{1.85}Ca_{0.15}CuO_{4-x}}$, are temperature dependent, and track the bulk spin susceptibility, in agreement with the measurements of Kitaoka *et al.*[20] for $\mathrm{La_{1.85}Sr_{0.15}CuO_{4-x}}$. A plot of the $\mathrm{CuO_2}$ planar oxygens' Knight shift in $\mathrm{La_{1.85}Ca_{0.15}CuO_{4-x}}$, shown in Fig. 1(d), versus the bulk susceptibility, is linear and the slope yields a value of $H_{\mathrm{hf}}=N\mu_B\Delta K/\Delta\chi_m=109\ \mathrm{kG}/\mu_B$ for the hyperfine coupling, similar to the value of $137\ \mathrm{kG}/\mu_B$ reported for $\mathrm{La_{1.85}Sr_{0.15}CuO_{4-x}}$.[20] Similar temperature-dependent behavior of the $\mathrm{CuO_2}$ planar oxygen has been observed for oxygen deficient samples of $\mathrm{YBa_2Cu_3O_{7-x}}$.[9,21,22] The frequency shifts of the apical sites of the lanthanum cuprates, $K\sim0.05\%$, are essentially temperature independent in both the normal and superconducting states.

Although the density of states at the Fermi level, $N(E_F)$, has been found by both theoretical calculations and by experiment to be oxygen $2p$-like,[23] from the relatively isotropic relaxation ($\mathbf{H}\|c$, $T_1\sim8.1\pm1$ ms; $\mathbf{H}\perp c$, $T_1\sim8\pm1$ ms, $12\pm1$ ms) of the $\mathrm{YBa_2Cu_3O_{7-x}}$ O(2,3) sites, and the small deviations from ideal Korringa behavior, the oxygens' relaxation appears to be dominated by the fractional $s$ character of the conduction band. The $2s$ hyperfine field is an order of magnitude larger than the $2p$. Hence, only a small fraction of $s$ character at the Fermi level can dominate the observed spin-lattice relaxation. However, for all the cuprates it seems plausible, due to their magnetic behavior, that there is an additional contribution to the spin susceptibility of the $\mathrm{CuO_2}$ planes, providing additional isotropic relaxation.

In Fig. 2(b) the relaxation rates of the lower-$T_c$ cuprates are shown. The $\mathrm{CuO_2}$ planar oxygen resonance of $\mathrm{Bi_2Sr_2CuO_{6+x}}$, which has a much lower critical temperature ($T_c=5.6$ K), is broader and more paramagnetically shifted than the $\mathrm{CuO_2}$ planar oxygen resonances of the other copper oxide materials, and was observed to broaden with decreasing temperature, in the normal state. This is in contrast to the $\mathrm{La_{1.85}Ca_{0.15}CuO_{4-x}}$ $\mathrm{CuO_2}$ resonance which actually narrows, from $\sim50$ kHz to $\sim32$ kHz linewidth at half-height, before the sample becomes superconducting. In addition to the contribution which is linear with temperature, there appears to be a temperature-independent component in the $\mathrm{Bi_2Sr_2CuO_{6+x}}$ relaxation and a value of $T_1T\sim3.7$ s K was extracted from a fit of the data to the expression $1/T_1=(aT+B)$. For $\mathrm{La_{1.85}Sr_{0.15}CuO_{4-x}}$ and $\mathrm{La_{1.85}Ca_{0.15}CuO_{4-x}}$, we measured the spin-lattice relaxation of the plane sites in the range of 300 to 100 K, since the apical O(2) and plane O(1) resonance lines begin to overlap below 100 K. In this range, the shift of the plane site of $\mathrm{La_{1.85}Sr_{0.15}CuO_{4-x}}$ decreases from $\sim0.17\%$ to 0.10% and $(T_1T)^{-1}$ is also observed to decrease slightly from $\sim0.3\mathrm{s^{-1}K^{-1}}$ to $\sim0.2\mathrm{s^{-1}K^{-1}}$. Likewise, the frequency shift of $\mathrm{La_{1.85}Ca_{0.15}CuO_{4-x}}$ decreases from $\sim0.14\%$ to $\sim0.09\%$. Although the scatter in our $(T_1T)^{-1}$ values for $\mathrm{La_{1.85}Ca_{0.15}CuO_{4-x}}$ and $\mathrm{La_{1.85}Sr_{0.15}CuO_{4-x}}$ is large, we find that the quantity $K_ST_1T$ is relatively constant. $K_S^2T_1T$, which should be constant for a Korringa-like relationship, decreases by $\sim50\%$. Similar behavior is observed for $\mathrm{YBa_2Cu_3O_{6.63}}$ where Takigawa *et al.* also find $K_ST_1T$ is constant.[21]

Millis, Monien, and Pines have developed a one component theory which describes the normal state of the cuprates as an "antiferromagnetic Fermi liquid" in which the spin susceptibility governing the nuclear spin-lattice relaxation consists of a Fermi liquid-like part and an antiferromagnetic part due to the coupling of the copper spins. It has been shown that this phenomenological model provides a quantitative fit of the relaxation data of the planar copper and oxygen sites in $\mathrm{YBa_2Cu_3O_7}$ (Ref. 24) and $\mathrm{YBa_2Cu_3O_{6.63}}$ (Ref. 25). Recently Monien *et al.*[26] have extended this model to $\mathrm{La_{1.85}Sr_{0.15}CuO_{4-x}}$

and determined the antiferromagnetic Fermi liquid parameters from our oxygen relaxation data along with the copper data of Kitaoka *et al.*[20] and Imai *et al.*[27] Our $^{17}$O spin-lattice relaxation results enable Monien *et al.* to calculate the antiferromagnetic correlation length, the characteristic spin fluctuation energy, and to rule out any appreciable departure from commensurability of the correlation peak at $Q=(\pi/a,\pi/a)$. Monien *et al.* conclude that at all temperatures, the antiferromagnetic correlations found in $La_{1.85}Sr_{0.15}CuO_{4-x}$ are stronger than those found in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.63}$. Their results,[26] and those of Millis *et al.*[24] and Monien *et al.*[25] suggest that both the spin and charge aspects of the normal-state properties of these cuprate superconductors can be quantitatively explained in terms of quasiparticles coupled to antiferromagnetic paramagnons.

The relaxation behavior of the lower-$T_c$ superconductors, $BaBi_{0.25}Pb_{0.75}O_3$ ($T_c=10$ K), and $BaSb_{0.25}Pb_{0.75}O_3$ ($T_c=2.6$ K), shown in Fig. 2(c), is also Korringa-like, but the nuclear spin-lattice relaxation times ($T_1T \sim 280$ s K and $\sim 400$ s K, respectively), are much longer than those of the cuprates, indicating these oxides to be much less metallic. This is also reflected in their oxygen frequency shifts ($K \sim 0.01\%-0.03\%$),[9] which are well within the diamagnetic frequency shift range for oxygen.[9] Similar behavior is observed for the BaO, TlO, SrO, and LaO planar oxygen sites of the cuprate materials, which have both small Knight shifts and relaxation rates. For example, preliminary estimates of $T_1$ of the BaO and TlO sites of $Tl_2Ba_2CaCu_2O_{8-x}$ indicate, at 300 K, $T_1 \gtrsim 0.5$ s, while the SrO site of $Bi_2Sr_2CaCu_2O_{8+x}$ has $T_1 \gtrsim 1.0$ s and the La(Sr)O site of $La_{1.85}Sr_{0.15}CuO_{4-x}$ has $T_1 \gtrsim 1.0$ s. Like the apical O(4) site in $YBa_2Cu_3O_{7-x}$, these oxide layers are at most only weakly coupled to the $CuO_2$ spin susceptibility in the normal state. This lack of metallic character has also been observed by $^{205}$Tl NMR of $Tl_2Ba_2CaCu_2O_{8+x}$,[28] which is neither Korringa-like in the normal state, nor has a significant Knight shift. Photoemission spectroscopy has also shown an alternation of metallic $CuO_2$ planes and insulating BiO and SrO planes in the bismuth material,[29] consistent with the general picture emerging from the NMR results. The potassium doped bismuthate, $Ba_{0.6}K_{0.4}BiO_3$ ($T_c=28$ K), has a somewhat larger frequency shift, $K_s \approx 0.05\%$,[9] and shorter spin-lattice relaxation time ($T_1T \sim 86$ s K).

As noted above, in the case of $Tl_2Ba_2CaCu_2O_{8+x}$, $YBa_2Cu_3O_{7-x}$, and $Bi_2Sr_2CaCu_2O_{8+x}$, the relaxation behavior may primarily reflect the fractional *s* state character of the conduction band. While it is generally believed that the total density of states at the Fermi level of both the cuprates and the bismuthates have substantial O2*p* character,[23] the relaxation rates of the oxygen sites of the bismuthates and the plumbate materials, with their smaller shifts and $1/T_1$ values, may be entirely due to the *p* contribution. We can obtain an order of magnitude estimate using the following expression for the spin-dipolar and orbital relaxation contributions for a *p* band:[30]

$$(T_1T)_p^{-1} = \left[\frac{52\pi k_B}{5\hbar}\right][\gamma_e\gamma_n\hbar^2 N(0)\langle r^{-3}\rangle]^2 . \tag{2}$$

Here $\langle r^{-3}\rangle$ is the average of $r^{-3}$ over the atomic oxygen 2*p* function and $N(0)$ is $\frac{1}{6}$ of the measured density of states, $N(E_F)$, due to the twofold spin degeneracy and threefold orbital degeneracy of the atomic *p* states.[31] This expression, derived by Obata using the tight binding approximation, is only strictly correct for ideal cubic symmetry. Using a value of 3.36 a.u. (Ref. 32) for $\langle r^{-3}\rangle$ and the measured $T_1T$ values, we find values of 0.09, 0.17, and 0.30 eV$^{-1}$ for $N(E_F)$ of $BaPbO_3$, $BaBi_{0.25}Pb_{0.75}O_3$ and $Ba_{0.6}K_{0.4}BiO_3$, respectively. The values derived from specific heat measurements are 0.18, 0.3, and 0.65 eV$^{-1}$.[33,34] Band structure calculations indicate that the oxygen 2*p* contribution is roughly one-half of the total density of states, that is, $N(E_F)_{O2p} \approx 0.12$ eV$^{-1}$ and $N(E_F)_{\rm total} \approx 0.24$ eV$^{-1}$ for $BaBi_{0.25}Pb_{0.75}O_3$,[35] and $N(E_F)_{O2p} \approx 0.26-0.32$ eV$^{-1}$ and $N(E_F)_{\rm total} \approx 0.46-0.72$ eV$^{-1}$ for $Ba_{0.6}K_{0.4}BiO_3$.[36] The agreement with the values calculated from the $T_1T$ measurement seem to be quite good.

The results presented thus far appear to fall into two classes: For the cuprates, the $CuO_2$ planes have large Knight shifts and correspondingly rapid relaxation rates, while the non-$CuO_2$ planar sites have small shifts and relaxation rates. In the copper-free materials, the shifts and relaxation rates are uniformly small, with the lowest-$T_c$ materials having the longest $T_1$ values and smallest shifts (from the normal diamagnetic range found in, e.g., $BaBiO_3$ or $BaPbO_3$). Perhaps notably, for $BaPbO_3$, the $T_1T$ value is 980 s K. Since it is thought by some workers that the low-$T_c$ oxides may be BCS superconductors, it seems reasonable to investigate which materials, if any, behave in the NMR experiment in a manner consistent with BCS theory.

We show in Fig. 3 the $(T_1T)^{1/2}$ values and estimated Knight shifts of a series of metal oxide superconductors, plotted as a function of their critical temperatures. A correlation of the Knight shifts and relaxation rates with $T_c$ is possible if the shifts and $(T_1T)^{1/2}$ values are tracking an increasing density of states at the Fermi level. The Knight shift is related to the electronic density of states through the conduction electron spins' susceptibility. In the independent-particle approximation, appropriate for simple *s*-band metals, the conduction electron spin susceptibility, $\chi_s$, is related to the density of states at the Fermi level by $\chi_s = 2\mu_B^2 N(E_F)$, where $\mu_B$ is the Bohr magneton. Since the Knight shift is defined as $K \equiv \Delta H/H = (8\pi/3)|\Psi_{(0)}|^2_{E_F}\chi_S$, it is also directly proportional to $N(E_F)$:

$$K = \frac{16\pi}{3}|\Psi_{(0)}|^2_{E_F}\mu_B^2 N(E_F) . \tag{3}$$

In addition to the Fermi contact term, there are also orbital and core polarization contributions to the total oxygen Knight shift, which appear to be small in the cuprates, as discussed previously. The shift for $Ba_{0.6}K_{0.4}BiO_3$ was estimated from the shift of the diamagnetic precursor compound, $BaBiO_3$ (0.0375% from $H_2O$) to be $\approx 0.05\%$.[9]

The relaxation rate of a metal is also proportional to the square of the electronic density of states at the Fermi

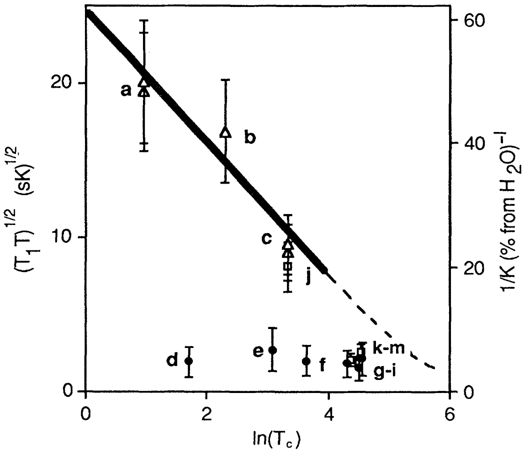

FIG. 3. $(T_1T)^{1/2}$ and $1/K$ as a function of the natural logarithm of the critical temperature, for a variety of oxide superconductors. $(T_1T)^{1/2}$ data for *a*, $BaSb_{0.25}Pb_{0.75}O_3$; *b*, $BaBi_{0.25}Pb_{0.75}O_3$; *c*, $Ba_{0.6}K_{0.4}BiO_3$; *d*, $Bi_2Sr_2CuO_{6+x}$; *e*, $La_{1.85}Ca_{0.15}CuO_{4-x}$; *f*, $La_{1.85}Sr_{0.15}CuO_{4-x}$; *g–i*, $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2CaCu_2O_{8+x}$, and $Tl_2Ba_2CaCu_2O_{8+x}$. $1/K$ values for *j*, $Ba_{0.6}K_{0.4}BiO_3$; and *k–m*, $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2CaCu_2O_{8+x}$, and $Tl_2Ba_2CaCu_2O_{8+x}$. The solid line is a weak coupling BCS curve and the dashed line is a strong coupling Kresin curve, scaled to a linear fit of the copper-free $(T_1T)^{1/2}$ results.

level, as in Eq. (2) for $(T_1T)_p^{-1}$. For *s* electrons, which couple to the nucleus through the Fermi contact interaction, the appropriate expression for the relaxation rate is

$$(T_1T)_S^{-1}=4\pi\gamma_n^2\hbar k_B\left[\frac{16\pi}{3}|\Psi(0)|^2_{E_F}\mu_B\right]^2[N(E_F)]^2 \; . \tag{4}$$

Since the exact orbital contributions to the total oxygen Knight shifts are not known, especially in the copper-free lower $T_c$ oxides, which have very small Knight shifts, the relaxation rates may more accurately reflect the actual trend in the density of states.

In weak coupling BCS-type superconductors, $T_c$ is related to the electronic density of states by

$$T_c \cong 1.14\Theta_D \exp(-1/\lambda), \text{ where } \lambda = VN(E_F) \; . \tag{5}$$

Here, $\Theta_D$ is the Debye temperature, $V$ is the effective pairing potential between electrons, and $\lambda<1$ for the weak coupling case. For $\lambda>1$ or strong coupling, this relationship breaks down and $T_c$ must be determined from numerical solutions of the Eliashberg equations. Kresin found the following analytical expression for any strength of the electron-phonon coupling parameter, $\lambda$:[37]

$$T_c=0.25\omega_D(e^{2/\lambda}-1)^{-1/2} \; , \tag{6}$$

where $\omega_D$ is a characteristic frequency describing the phonon spectrum. In Fig. 3 we show weak coupling and Kresin-BCS curves appropriately scaled to fit the data for the copper-free materials. Due to the scatter in the reported values, we did not incorporate the Debye temperatures and effective pairing potentials into Fig. 3. For any reasonable values of $\Theta_D$ for the copper-free oxides, the relaxation and frequency shift values are consistent with a BCS-like relationship between the density of states at the Fermi level, and $T_c$. There is no similar correlation for the cuprates. This could reflect the possibility that the spin susceptibility of the $CuO_2$ planes does not reflect only the density of states at the Fermi level.

In summary, the metallic character of the $CuO_2$ planes in the yttrium, thallium, and bismuth copper oxide superconductors is manifest in the nearly ideal Korringa behavior of these oxygen sites, with the *s*-contact interaction dominating the relaxation. The other oxide planes are more insulating, with much longer $T_1$ values, and frequency shifts in the diamagnetic shift range for oxygen. The oxygen site of the bismuthate (plumbate) superconductors also show weak metallic behavior, with $T_1$ values and frequency shifts of the same magnitude as the copper-free oxide planes of the cuprates. The Knight shifts of the $CuO_2$ planes in the thallium, yttrium, and bismuth cuprates contain large spin contributions which are temperature independent in the normal state and vanish as the materials become superconducting. The Knight shifts of the $CuO_2$ plane sites of $La_{1.85}Sr_{0.15}CuO_{4-x}$ and $La_{1.85}Ca_{0.15}CuO_{4-x}$ are temperature dependent in the normal state, and both systems strongly resemble the behavior found in $YBa_2Cu_3O_{6.63}$.[21] While the $(T_1T)^{-1}$ values of the cuprates do not vary significantly with $T_c$, our results on the three copper-free oxide superconductors appear consistent with a BCS-like relationship between $N(E_F)$ and $T_c$.

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