PHYSICAL REVIEW B **90**, 014405 (2014)

Short-range magnetic interactions and optical band-edge physics in $SrCu_2(BO_3)_2$

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(Received 1 November 2013; revised manuscript received 7 May 2014; published 7 July 2014)

Optical reflectivity spectra of $SrCu_2(BO_3)_2$ revealed a feature at 1.5 eV assigned as the energy gap for the charge-transfer excitation. Changes in the optical reflectivity induced by temperature and applied magnetic field were compared to population statistics to establish a correlation between the optical changes and magnetic excitations on the dimers. A Curie-like analysis of the optical data demonstrated that the Weiss constant and spin-gap energy obtained from an analysis of the magnetic susceptibility could also be used to describe reflectivity changes at the band edge. Differences between the temperature- and magnetic field-induced changes to the optical data were also identified and interpreted as potentially indicative of a multitriplet or cooperative interaction between dimer spin excitations and band-edge charge carriers.

DOI: 10.1103/PhysRevB.90.014405 PACS number(s): 75.10.Jm, 71.27.+a, 78.20.Ls, 78.67.−n

I. INTRODUCTION

Spin systems characterized by either frustration or reduced dimensionality have garnered wide interest due to their ability to exhibit novel quantum phenomena such as superconductivity [1,2], spin-liquid phases [3], and gapped spin-excitations [4] (e.g., Haldane [5], spin-Peierls [6], etc.). $SrCu_2(BO_3)_2$, or SCBO, a close experimental realization of the Shastry-Sutherland model, is one such quantum system in which the singlet ground state is separated from the excited triplet state by an energy gap (∼35 K) [7–10] that can be closed by high magnetic fields (>20 T) [11,12]. The $S = 1/2$ copper ions form a two-dimensional (2D) network of perpendicular spin dimers with competing intradimer (J) and interdimer (J') exchange interactions resulting in a highly frustrated quantum spin system [Fig. 1(a)]. The ratio of these interactions may place SCBO in the proximity of a quantum critical point separating a gapless, long-range antiferromagnetic (AFM) Néel state from an exact singlet dimer state [12].

High magnetic field magnetization measurements of SCBO reveal a series of plateaus, which occur when the magnetic field-tuned density of triplets becomes commensurate with the lattice periodicity [9,13–17]. This unusual behavior is thought to arise due to a competition between the kinetic energy and repulsive interactions of the bosonic triplet excitations [13,18]. These triplets also have been observed to form ordered stripelike patterns, which mimic structures similar to those predicted by the Hofstadter butterfly energy spectrum for confined fermions [16,19]. Further, it has been demonstrated that the singlet-triplet gap can be closed under high enough pressures [20]. Due to these unusual magnetic properties, extensive research has been performed to understand the behavior of this low-dimensional magnet under various conditions [21–32].

II. MOTIVATION

Since SCBO demonstrates such a rich spectrum of spin-related physics, it is a natural extension to consider whether these magnetic effects might have an influence on the optical properties of this complex oxide. An intriguing and significant aspect of strongly correlated physics concerns the coupling of optical frequency charge excitations with lower energy excitations (sometimes lower by orders of magnitude) within the orbital, spin, or lattice degrees of freedom. One example is a change in the optical spectrum that occurs in tandem with a magnetic field-induced phase change [33,34]. In general, a connection between changes in optical properties and magnetic excitations has been observed and reported in other complex oxides such as manganites [35–38] and other cuprates [39–42]. SCBO presents an important opportunity to explore charge-spin dependences in a two-dimensional copper oxide because the spin order is short range and excitations are highly localized [10]. As a result, there is the potential for observing unique optical responses to tuning the population of magnetic excitations, to forming magnetic bound states, or to other excited-state interactions. In conjunction with its inherently short-range magnetic character, SCBO is also expected to lie near a quantum phase transition to a long-range ordered AFM phase. Therefore, SCBO is an important system for investigating the ways in which short-range spin correlations might influence the physics of band-edge charge carriers introduced either by doping or optical injection. The knowledge gained from such a model system further has general significance in helping to elucidate the role of short-range spin correlations within insulator-metal transitions in oxides.

III. RESULTS AND DISCUSSION

A. Sample characterization: Magnetic susceptibility

To look for correlated charge-spin behaviors in SCBO, we measured its linear optical reflectivity while separately varying temperature and applied magnetic field. In preparation for the measurements, crystals of SCBO were grown in a floating zone furnace and samples for optical measurements were cut and polished. Characterization of the samples by magnetic

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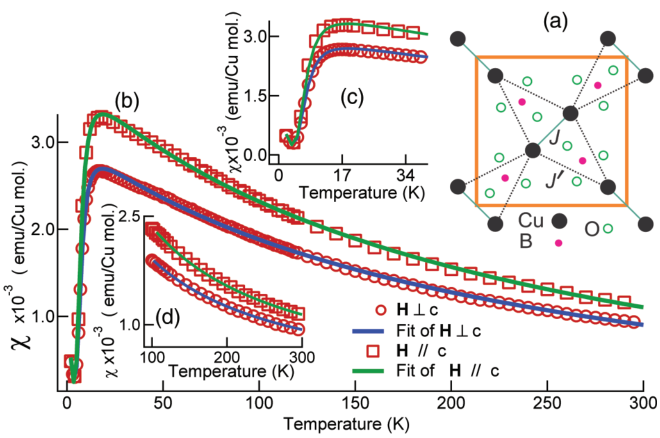

FIG. 1. (Color online) (a) Two-dimensional structure of SCBO projected along the *ab* plane showing the perpendicular network of Cu dimers with intradimer (J) and interdimer (J') exchange interactions. The square represents a tetragonal unit cell. Magnetic susceptibility of SCBO: (b) from 2–300 K with an interacting dimer model fit, (c) in the spin-gap regime showing a rapid fall below 17 K, and (d) from 100–300 K with a Curie-Weiss model fit.

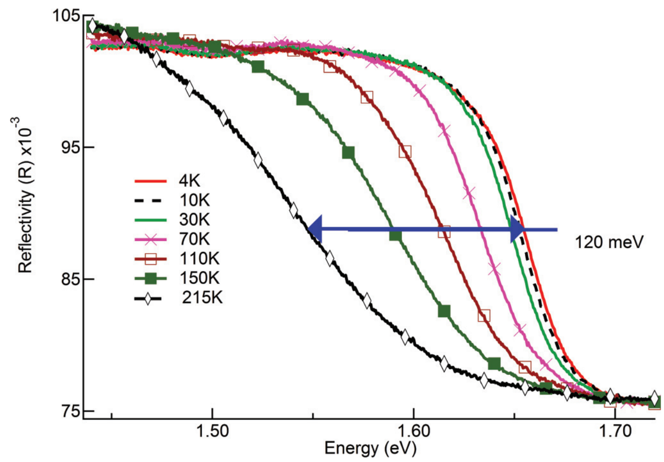

FIG. 2. (Color online) Reflectivity of SCBO from 4 K to 215 K showing the band-edge changes.

susceptibility measurements at 0.5 T exhibited features typical of a frustrated spin dimer [Fig. 1(b)]. A rapid decrease in the magnetic susceptibility below 17 K [Fig. 1(c)] signaled the decline of triplet excitations as a result of the singlet-triplet energy gap. Figure 1(d) shows the high-temperature magnetic susceptibility in the 100–300 K range fitted to a Curie-Weiss model, $C/(T-\Theta)$, with $C = Ng^2\mu_B^2 S(S+1)/3k_B$ [9]. Here N is the Avogadro number, g is the g factor, μ_B is the Bohr magneton, k_B is the Boltzmann constant, and Θ is the Weiss constant. In these fits, the Weiss constant was found to be -88 K ($\mathbf{H}\|c$) and -91 K ($\mathbf{H}\perp c$), which was similar to prior reports [9,11]. The g-factor values extracted from these fits, 2.17 for $\mathbf{H}\|$ and 1.97 for $\mathbf{H}\perp$, agreed strongly with those determined by ESR measurements [29]. In Fig. 1(b), the magnetic susceptibility curve from 2 K to 300 K was fitted with an interacting spin-dimer model having an additional Curie term to account for the upturned tail below 4 K [43],

$$\chi = C_1 + \frac{C_2}{(T-\Theta_{4\mathrm{K}})} + \frac{C_3}{T(3+\exp(\Delta/T)+\Phi/T)}. \quad (1)$$

In this model Δ is the gap parameter, $\Theta_{4\mathrm{K}}$ is the Weiss constant for the 4 K tail, and Φ represents the interaction between dimers. For both orientations, Δ was found to be 37.1 ± 0.3 K, which agreed closely with the spin-gap values measured previously [9,10,44]. Φ, which can be regarded as an effective interdimer interaction due to various next-nearest dimer spins, was found to be 888 K ($\mathbf{H}\perp$) and 879 K ($\mathbf{H}\|$) [43,45–47]. In systems where an interdimer exchange interaction comparable to the intradimer exchange is present, a mean-field description is often incapable of providing accurate interdimer interaction energies [47,48].

B. Optical reflectivity

Optical reflectivity of SCBO, [$\mathcal{R}(w)$], in the range of 1.25 eV to 2.17 eV, was measured from 215 K to 4 K using a fiber-based probe cooled inside a Janis ^{4}He cryostat. A quartz-tungsten-halogen lamp was used as an excitation source ($\mathbf{k}\perp c$ axis) and the reflection from a silver mirror was used as a reference. Between 1.40 eV and 1.70 eV (Fig. 2), the reflectivity underwent a significant decrease (27% change). As the temperature was lowered, the edge of the reflection feature became steeper and shifted towards higher energy. This temperature dependence was typical of the conduction band edge in semiconductors and other copper oxides [39,41,49–51]. The edge feature can be further interpreted on the basis of LDA+U calculations [52]. The hybridization between copper $3d_{x^2-y^2}$ and oxygen $2p_x$ and $2p_y$ orbitals produces states near the Fermi energy. Due to strong on-site electron-electron interactions (i.e., $U_{\mathrm{eff}} = 4$ eV), the $3d_{x^2-y^2}$ states are split into lower and upper Hubbard bands with the oxygenlike $2p$ band between them. Thus, SCBO is considered a charge-transfer (CT) insulator with a gap of about 1.5 eV, which is close to the observed reflectivity edge. Therefore, we assigned the observed feature as the optical edge of the upper Hubbard band (UHB).

The large temperature-induced variation in reflectivity revealed a large band-edge energy shift of 120 meV shown in Fig. 2. While this shift was in a direction consistent with an interpretation based on thermal expansion and contraction of the lattice, the size of the shift was significantly larger than those normally observed in nonmagnetic semiconductors [53–55]. A similar enhancement to the band-edge shift has been observed in several other magnetic semiconductors and attributed to magnetic ordering. For example, optical spectra of CuO have shown a large band-edge shift and deviation from the Varshni model that describes the temperature dependence of classical semiconductors [39,49,56]. Deviation from the Varshni model has even been suggested as an indication of magnetic ordering [39,57]. Additionally, Rocquefelte *et al.* linked the band-edge contraction in CuO to a change in the spin order using first-principles calculations based on density functional theory [58]. While SCBO exhibits no long-range spin ordering, it shares several other important attributes with CuO and related copper oxide systems among which are: being a CT insulator, having 2D copper oxide planes [59], and $d_{x^2-y^2}$ contribution to the UHB. Since spin correlations in SCBO are restricted to short-range dimer interactions, changes in the reflectivity occurring at temperatures or magnetic fields that are also significant for dimer excitations could demonstrate a potential interdependence between short-range magnetic correlations and the physics of band-edge charge carriers.

Other oxides have also shown large band-edge shifts, which were attributed to band-gap renormalization resulting from electron-phonon interactions and changes in the spin order [39,41]. Strong enhancement of spectral weight transfer with the onset of a long-range AFM ordered phase was also observed in $LaMnO_3$ [38]. In the reflectance spectra of $Sr_2CuO_2Cl_2$, as the temperature was increased, the peak at 2 eV showed a reduction in reflectance and the peak position and edge shifted (∼150 meV) towards lower energies [41]. These significant changes in the reflectance were suggested to have occurred due to the changes in the spin ordering as the temperature was increased. The electron-hole pairs created in this charge-transfer transition were proposed to result in the formation of a Zhang-Rice band (ZRB). Since the proposed ZRB would be strongly hybridized to the Cu orbitals, changes in spin ordering were thought to influence the ZRB thereby producing the significant band-edge shift [41].

In $CuGeO_3$, a spin-Peierls material with Cu-O chains, absorption spectra showed a strong redshift of the absorption edge (160 meV) when temperature was increased and this charge-transfer transition was also proposed to yield a Zhang-Rice-like excitation [42]. The absorption edge remained constant till 60 K beyond which it underwent significant reduction. Interestingly, the maximum in the temperature dependence of the magnetic susceptibility also occurred at about 60 K (a rapid decrease of susceptibility happened below 14 K) [6,42]. All together, these similarities invited a comparison in SCBO between its optical and magnetic properties in order to explore magnetic interactions as a factor in the large band-edge shift observed. Based on these aforementioned evidences, it is possible that the significant band-edge shift observed in SCBO could be connected with spin interactions on the dimers. Since the O 2*p* and Cu 3*d* orbitals are strongly hybridized [52], magnetic excitations on the copper sites might have an influence on the band edge.

Measurements of optical spectra and magnetic susceptibility can reveal information about changes in electronic and magnetic state populations, respectively. Accordingly, the high-temperature magnetic susceptibility of SCBO conformed well to a Curie law having a Weiss temperature similar to prior reports. Additionally, the low-temperature susceptibility fitted well to a trend based on Boltzmann counting statistics involving a single ground state and a triply degenerate excited state [Eq. (1)]. This trend further reported an accurate spin-gap energy. If changes in the optical spectra correlate with magnetic excitations on the dimers, then it is reasonable to investigate whether or not the observed changes in the optical reflectivity also can be described by a similar statistical treatment. This type of approach has been previously employed in studies of spin dimers in organic biradicals, for example [60,61]. In this case, the change in absorption was compared with the population statistics of excited dimers. Similar comparisons are also regularly used in EPR studies of magnetic dimers where the absorption intensity is often fitted by the fractional triplet population density multiplied by a $1/T$ Curie susceptibility, typically cited as the Bleaney-Bowers (B-B) equation [47,62–65]. Following these precedents, one might expect that the change in reflectivity at the band edge in SCBO could also be described by a similar type of population analysis that may additionally share similarities with the analysis performed for magnetic susceptibility.

C. Magnetic field dependence of optical reflectivity

In order to test this reasoning, we decided to measure the magnetic field-induced change in reflectivity at low temperature. As a magnetic field is applied, the spin gap is closed and triplet excitations appear on the magnetic dimers. Thus, applying magnetic field at a low, fixed temperature is a way to control the type of spin correlations that appear on the dimers. If the reflectivity near the band edge is correlated with the population of triplet excitations, then a fit of the intensity change to a statistical population description for a two-level system should reveal an energy gap that matches the observed singlet-triplet splitting in SCBO.

The magnetic field dependence of the sample reflectivity (**H**, **k**$\perp c$ axis) was measured at 1.6 K from 0 T to 35 T at 2 T intervals using the 35 T resistive magnet at the National High Magnetic Field Laboratory in Tallahassee. In Figs. 3(a)–3(b) the change in reflectivity was zero at lower fields and started decreasing only beyond 20 T. Magnetization measurements also showed a similar behavior [Fig. 3(c) inset], where the critical field was estimated to be between 21–22.5 T [9,11]. Figure 3(d) shows the energy diagram for Zeeman splitting

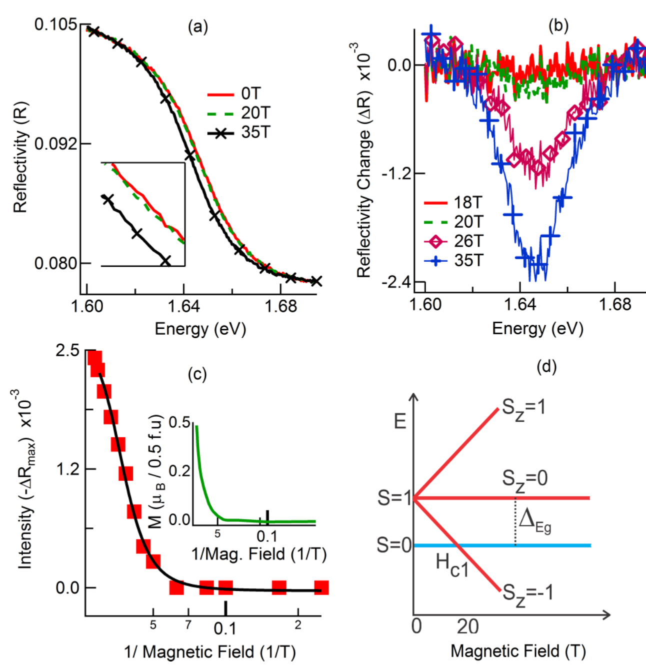

FIG. 3. (Color online) (a) Magnetic field dependence of reflectivity at 0 T, 20 T, and 35 T. Inset shows a close-up view. (b) Magnetic field dependence of the reflectivity change $\Delta\mathcal{R}(B) = [\mathcal{R}(\mathrm{B}) - \mathcal{R}(0\ \mathrm{T})]$. (c) $-\Delta\mathcal{R}_{\max}(B)$ magnetic field dependence. The solid line is a fit using Eq. (2). High field magnetization measurements up to 30 T are shown in the inset for comparison [66]. (d) Zeeman splitting of a singlet-triplet spin system demonstrating the energy gap, Δ_{Eg}.

of the triplet degeneracy. At the critical field, the $S_z = -1$ triplet branch became the lowest energy level, resulting in the creation of triplets and a nonzero magnetization. This singlet-triplet level crossing was clearly exhibited in our optical reflectivity data [Fig. 3(c)] similarly with previously reported magnetization studies [9,11,66] and provided strong evidence of a correlation between electronic structure and spin excitations.

To extract the characteristic parameters of the system, we fitted the magnetic field-induced reflectivity change, $I = -\Delta\mathcal{R}_{\max}(B)$, with a noninteracting dimer model in which the gap parameter was tuned by the applied magnetic field. The fit function was,

$$I \propto \frac{C_4}{T\left[1+\exp\frac{-g\mu_B B}{T}\left(1+\exp\frac{-g\mu_B B}{T}+\exp\frac{\Delta_1}{T}\right)\right]}. \tag{2}$$

This equation was the result of a simple application of Boltzmann counting statistics for a two-level system of magnetic dimers. The value of the fitting parameter Δ_1 was found to be 3.09 meV (35.9 K), which matched well to prior reports of the spin-gap energy. The behavior of reflectivity with applied magnetic field clearly demonstrated that the optical band-edge reflectivity was correlated with lower energy magnetic excitations in SCBO.

D. Temperature dependence of optical reflectivity

Dimer spin excitations in SCBO can be controlled by temperature as well as by magnetic field [20,21]. The temperature-dependent magnetic susceptibility in Fig. 1 was fitted by a Curie-like dimer susceptibility having a singlet-triplet energy gap of 37 K. Since the magnetic field-tuned reflectivity demonstrated a close similarity to the statistics of magnetically tuned dimer excitations, we also investigated the use of a similar temperature-dependent population trend to describe the temperature-tuned changes in reflectivity. The temperature-induced change in reflectivity [Fig. 4(b)], obtained using a 4 K reference [Fig. 4(a)], was initially compared with a Curie-Weiss trend [green line in Fig. 4(b)] having the same Weiss constant obtained from the magnetic susceptibility data in Fig. 1(d). This comparison demonstrated general agreement,

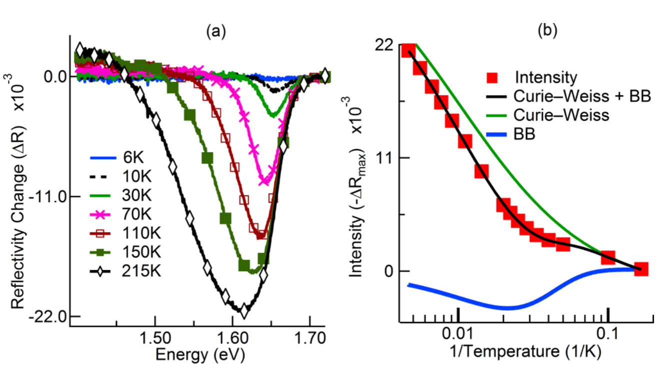

FIG. 4. (Color online) (a) Temperature-induced change of the reflectivity $\Delta\mathcal{R}(T) = [\mathcal{R}(T) - \mathcal{R}(4\text{ K})]$. (b) $-\Delta\mathcal{R}_{\max}(T)$ temperature dependence showing the two-component Curie-Weiss and Bleaney-Bowers fit (BB).

but could not reproduce the detailed behavior of the reflectivity over the entire temperature range.

Next, we added a Bleaney-Bowers dependence to the initial Curie-Weiss trend and obtained the following expression for intensity, $I = -\Delta\mathcal{R}_{\max}(T)$;

$$I \propto \frac{C_5}{(T-\Theta_2)} + \frac{C_6}{T[3+\exp(\Delta_2/T)]}. \tag{3}$$

The result of this fit is shown in Fig. 4(b) (black line). As with the magnetic field-tuned reflectivity data, the dimerlike population model reproduced the temperature dependence of the reflectivity very well. Nonetheless, the fitting parameter describing the singlet-triplet gap (Δ_2) reported a value of 75 K, approximately twice the size of the usual singlet-triplet gap.

Though the magnetically tuned reflectivity was primarily correlated with the singlet-triplet population ratio, it was clear that the temperature-tuned reflectivity correlated with some other process occurring at an energy approximately twice that of the spin gap. In the case of the magnetically tuned reflectivity, $-\Delta\mathcal{R}_{\max}(B)$ increased thereby widening the band as triplet excitations appeared. However, in contrast to this result, the portion of the $-\Delta\mathcal{R}_{\max}(T)$ that was fitted by the dimerlike susceptibility trend exhibited a decrease, resulting in a contraction of the band edge [blue line in Fig. 4(b)]. Based on the results obtained using a magnetic field to tune the triplet population at 1.6 K, it was clear that a contraction of the band edge occurred with the onset of AFM intradimer spin correlations. If a similar connection between optics and dimer excitations can be maintained to higher temperatures, the temperature-tuned reflectivity suggested that short-range AFM spin correlations may have a significant impact on the band edge at temperatures significantly higher than the spin-gap energy. In summary, the good fit obtained by Eq. (3) demonstrated that the temperature-tuned reflectivity could be described by population statistics involving a ground and degenerate excited state. However, the failure of the fitting to reproduce the correct spin-gap energy made it clear that physics beyond intradimer spin correlations was significant.

Our analysis has demonstrated that the temperature and magnetic field dependences of the reflectivity can be described by population statistics, which bear striking resemblances to those used to describe the magnetic susceptibility. However, the energy gaps that described the intensity changes were different depending on which variable, either magnetic field or temperature, was tuned. In the case of magnetic field, the gap energy matched the usual singlet-triplet gap, and the band edge expanded with the appearance of triplet excitations. On the other hand, the temperature dependence of the reflectivity yielded a gap energy approximately twice this value, and the band-edge contraction was enhanced beyond the Curie trend at temperatures above the spin-gap energy. One way to reconcile the two contrasting results induced by magnetic field and temperature is to postulate that the temperature dependence of the reflectivity was additionally sensitive to a second excited state, above the usual singlet-triplet gap, that was not accessed in the magnetic field-tuned data. If one rewrites Eq. (3) to incorporate a second, higher excited state, then the intensity, $I = -\Delta\mathcal{R}_{\max}(T)$ can be expressed using Eq. (4) in which the first and the second terms are the Curie-Weiss and B-B contributions, respectively.

$$I \propto \frac{C_7}{(T-\Theta_3)} + \frac{C_8}{T\left[D_u + \exp\left(\frac{\Delta_u}{T}\right) + 3\exp\left(\frac{\Delta_u-\Delta_t}{T}\right)\right]}. \quad (4)$$

The terms Δ_u and D_u are the gap energy and degeneracy, respectively, of the higher-temperature excited state in the B-B contribution. Δ_t is the energy of the usual singlet-triplet gap. In this formulation, in addition to the triplet state, an allowance was made for a second, higher excited state. In this way, the population was distributed between three levels. The higher energy gap parameter Δ_u ranged from 76.5 ± 1.2 K when $D_u = 1$ to 85.6 ± 1.0 K when $D_u = 5$, which was consistently larger than the singlet-triplet gap from the magnetic susceptibility by at least a factor of two. Δ_u was allowed to vary in order to account for the effects of degeneracy. The fit was indistinguishable from the one shown in Fig. 4(b). This three-level formalism produced a fit of the temperature-induced intensity change that took into account the usual singlet-triplet gap.

The results of fitting the temperature-tuned reflectivity implied that there could be an excited state of the dimers at roughly twice the singlet-triplet gap that might involve short-range antiferromagnetic spin correlations. If so, this potential excited state could exist as a multitriplet bound state, in which multiple dimers form an overall singlet state. The existence of multitriplet bound states has been well established via neutron scattering [10,21], EPR [28,67], and Raman [22] studies, and the fitted gap energy was well within the spectrum of two and three triplet bound states. The very narrow dispersion of lone triplet excitations leads to the formation of triplet bound states, which can more easily hop from site to site within a perturbation theory framework [10,12]. Though these multitriplet complexes have been observed, they do not affect the magnetic susceptibility as significantly as intradimer AFM correlations do below 17 K. Therefore, it is not clear why such a multitriplet state, if indeed responsible, should have such a significant influence on the reflectivity. The reflectivity is nonetheless influenced strongly at higher temperatures, while the magnetic susceptibility suggested that the number of AFM correlations at these temperatures would be small compared to the overall paramagnetism. Since the reflectivity cannot be measured without photoexcitation, it is additionally possible that the introduction of charge carriers near the band edge via photoexcitation could have an influence on the optical data that would not otherwise be captured in magnetic susceptibility. For example, Zhang-Ng excitons were proposed in materials such as $Sr_2CuO_2Cl_2$ and $CuGeO_3$ as the reason for the significant temperature dependence of their optical spectra [41,42].

The temperature dependence of the reflectivity significantly revealed that a part of the intensity change was nonmonotonic with temperature. In the magnetic field-tuned optical data, $-\Delta\mathcal{R}_{\max}(B)$ monotonically progressed from low intensity at zero and low magnetic fields to high intensity at magnetic fields above the spin-gap energy. In such a way, apart from the obvious saturation expected at ultrahigh magnetic fields, the band-edge expansion was monotonic with increasing triplet densities up to the highest magnetic field accessible. In contrast, although the overall band-edge contraction in the temperature dependence was monotonic with decreasing temperature, the dimerlike contribution produced a significant enhancement to the band-edge contraction at temperatures above the triplet excitation gap that went away at the lowest temperatures instead of continuing to increase. Since this was an enhancement to the band-edge contraction and occurred at twice the spin gap, it should not be due to lone triplet excitations or intradimer AFM correlations. Based on the magnetic susceptibility, one also would not have anticipated such a significant nonmonotonic contribution to the band-edge contraction at these temperatures due to dimer interactions. Nonetheless, the optical data is still well described by a statistical population analysis with parameters that match energy scales measured in the magnetic susceptibility.

IV. CONCLUSION

To conclude, a 1.5 eV reflectivity feature was measured in SCBO using linear optical reflectivity techniques. This feature was assigned as the edge of the UHB based on prior published first-principles calculations. The reflectivity in this range underwent large changes as temperature and magnetic field were varied. Spectral changes in the optical reflectivity induced by magnetic field clearly demonstrated that the magnetically tuned band-edge contraction correlated with the singlet-triplet population ratio. Optical changes with temperature were also fitted by population trends that could indicate the influence of a dimer-related spin excitation at temperatures above the usual spin-gap energy. Together, the results demonstrated a strong correlation between spin excitations and optical band-edge excitations in SCBO.

ACKNOWLEDGMENTS

This work was conducted at the National High Magnetic Field Laboratory, which is supported by the NSF through NSF-DMR-0084173 and the State of Florida. J.G.C. and T.D.T. were supported by a User Collaboration Grant (UCGP).

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