Magnetothermal behavior of the two-dimensional triangular-lattice compounds $RCuO_2$ [R = La, Pr, Nu, Eu, and ($La_{0.2}Gd_{0.8}$)]

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The magnetothermal properties of the Delafossite-type compounds $RCuO_2$, with R = La, Pr, Nd, Eu,and $La_{0.2}Gd_{0.8}$ are presented. Particular attention is paid to the low-temperature cooperative behavior of this planar triangular system. Frustration is found to exist for the Kramers-ion compounds. For $R = La_{0.2}Gd_{0.8}$, a spin-glass-like behavior is found.

The discovery of high-temperature superconductivity (HTS) in layered cuprates has invigorated the study of cooperative properties in two-dimensional (2D) magnets.[1] This was motivated in part by Anderson's early conjecture[2] that HTS was an example of resonating-valence-bond[3] (RVB) behavior in a 2D Heisenberg antiferromagnet (AF) when doped away from half-filling. In the insulating phase, the RVB state, as originally described, is comprised of spins which are paired in a dynamic, or resonating, singlet (spin-Peierls) state, the classical Néel state being destabilized by quantum fluctuations. Subsequent theoretical work[4] brought attention to the fact that, quite apart from the central question of electron transport in the doped system, much remained to be understood about quantum effects in the insulating 2D Heisenberg AF. In particular, it was shown that the temperature dependence of the correlation length[5] in the HTS parent compound La_2CuO_4 was consistent with Néel order at $T=0$ and not with a RVB type of state.

Despite the inapplicability of the RVB state to La_2CuO_4, it is an interesting model which calls for experimental realizations. The distinguishing characteristic of such a state, namely, the absence of long-range (Néel) order, arises directly as a result of *geometrical frustration*[6] of the spin-spin interactions. This is to be contrasted with that in typical spin-glass materials,[7,8] in which frustration is induced by site disorder. The prototype for discussing geometrical frustration is a 2D triangular-lattice Ising AF. Here the cause of frustration is clear—collinear AF order is incompatible with a nonbipartite lattice and, as a result, the system is disordered even at $T=0$. For real systems, however, the application of Ising spins is restrictive. Most spin systems have vector character and Huse and Elser[9] have shown that the Heisenberg version of the 2D triangular-lattice AF does indeed have long-range order at $T=0$. Nevertheless, there still seems to exist the possibility that a RVB-like state can exist in a real system at least in a limited temperature range and, given the paucity of triangular-symmetry antiferromagnetic compounds, a search for compounds of this type seems warranted.

That triangular-symmetry antiferromagnets have unusual ground states has been known for some time, at least since the work of Wannier.[10] Specifically, he showed that the Ising case did not possess an ordered state at $T=0$, having instead an entropy of $S_0 = 0.323R$, where R is the gas constant. Such a suppression of the ordering temperature, T_c, is a general effect of frustration, consistent with the two-spin correlation length remaining finite, as the temperature is lowered. The suppression of order by frustration is to be distinguished from suppression due to "rarefication," i.e., reduction of the number of nearest neighbors, either by random dilution,[11] or by the ordered type of dilution which occurs in a quasi-low-dimensional system. In rarefied systems,[1,12] the correlation length grows as the temperature is lowered only to the spatial extent allowed by the geometrical constraints. Nevertheless, the susceptibility digresses from the high-temperature Curie-Weiss behavior on much the same temperature scale as the analogous dense system, and this digression will in general occur well above the mean-field T_c. On the other hand, in frustrated systems, because the correlation length remains small, the susceptibility will obey a Curie-Weiss form down to below the Curie-Weiss temperature, Θ_{CW}.

Following the above line of reasoning, highly geometrically frustrated materials should obey the following criteria: First, they should have ordered, concentrated arrays of spins situated on a frustrating lattice. Second, Curie-Weiss behavior should extend to temperatures below Θ_{CW}, thus allowing a faithful determination of Θ_{CW}. Lastly, ordering, at temperature T_c, should not occur until $T_c \ll \Theta_{CW}$. In order to compare the degree of frustration in different materials, it is convenient to define the ratio $f = \Theta_{CW}/T_c$.

Although Anderson's RVB theory provides much of the motivation for investigating triangle-based compounds, for such systems there is in fact a plethora of predicted phenomena, which, while not explicit related to a RVB state, nevertheless have their origins in frustration. These include various topological excitations,[13] phase diagrams,[14] and critical behavior characterized by nonuniversality.[15] Most of the relevant experimental work has involved iron-group transition-metal compounds,[16] such as the vanadium dihalides[17] and various chromium compounds[18] with triangle-based lattices. There is, however, a special interest which is attached to

rare-earth analog of these materials. Rare-earth ion groups interacting via superexchange typically have much smaller interaction strengths, owing to a smaller radial extent of the valence electrons, compared with iron-group elements. Thus cooperative phenomena in corresponding rare-earth crystals occur at much lower temperatures, usually in the liquid-helium range. There are two benefits to this. The first is that thermodynamic information about the magnetism will be easier to obtain since the specific heat will not be dominated by phonons. The second is that cooperative behavior will be alterable by attainable magnetic fields, allowing the study of competing effects of frustration and field for raising the spin degeneracy.

In the present work is described the synthesis and characterization of the Delafossite-type rare-earth compounds. These materials, $R\mathrm{CuO_2}$, crystallize in a simple triangular structure with rhombohedral space group[19] $R\bar{3}m$ (D_{3d}^5), and are insulators. R is an early-rare-earth ion and lies in layers separated by nonmagnetic Cu^{1+} sheets. In the present study, R=La, Pr, Nd, Eu, and $\mathrm{La_{0.2}Gd_{0.8}}$. The cations form triangular sublattices stacked along the c axis in a three-layer repeat sequence *ABCABC*. The oxygen atoms stack differently in an *AABBCCAA* sequence, resulting in a different coordination for the R and Cu atoms. As expected, the monovalent Cu is linearly coordinated by two oxygen atoms, whereas the R atom is at the center of a distorted oxygen octahedron. A view of the structure, showing the O octahedra and Cu atoms, is shown in Fig. 1. In $\mathrm{LaCuO_2}$, the average La-O distance is equal to 2.43 Å and the nearest-neighbor (NN) La-La distance is 3.83 Å (six intraplane NN's). The next-nearest-neighbor (NNN) distance is 6.11 Å (six interplane NNN's), followed by 6.63 Å (six intraplane NNN's). A pronounced difference exists between the Néel and NNN distances. Given the usually strong distance dependence of the two main interactions (superexchange and dipole-dipole), the intraplane interactions will certainly dominate and the expected behavior is that of a quasi-2D magnet.

All samples were prepared in powder form, starting from the respective sesquioxides R_2O_3 and $\mathrm{CuO_2}$. The starting materials were well mixed and then heated in evacuated quartz ampoules at temperatures around 900 °C. Single-phase powders of $R\mathrm{CuO_2}$ were obtained after regrinding and reheating twice to ensure homogeneity. X-ray powder spectra were taken after the final heat treatment, and lattice parameters were refined (Table I). High-quality samples were thus obtained for the early rare earths Pr, Nd, and Eu. For Gd concentrations up to 80 at. %, single-phase material was obtained. However, for higher Gd concentrations, and for the later rare earths, multiphase material was obtained, presumably as a result of a steric constraint. For Sm, complicated behavior was found in the susceptibility, suggesting the presence of an inhomogeneous mixed-valence material, arising from the presence of both Sm^{2+} and Sm^{3+} ions.

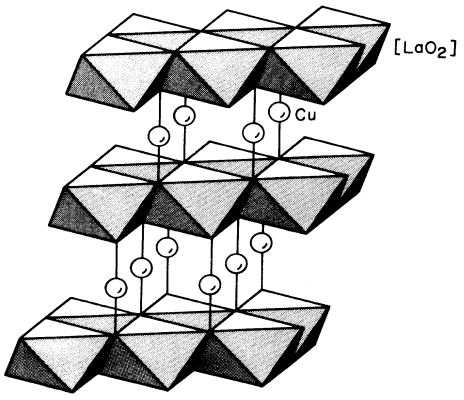

FIG. 1. View of the Delafossite-type structure for $R\mathrm{CuO_2}$. RO_6 octahedra and Cu atoms are depicted.

Magnetization (M) measurements were carried out with use of a commercial superconducting quantum interference device (SQUID) magnetometer in the temperature range 2–300 K and typically in applied fields $H \leq 0.1$ T. The dc susceptibility $\chi(T)$ was taken to be M/H in this field range. Specific-heat (C) data were obtained with a standard semiadiabatic heat-pulse technique. ac susceptibility (χ_{ac}) was obtained with use of a mutual-inductance technique.

The susceptibility for the nonmagnetic end member $\mathrm{LaCuO_2}$ can be described by the sum of a constant diamagnetic contribution of $\chi_{dia} = -1.7\times10^{-5}$ and a small Curie-like upturn at the lowest temperatures. The upturn is most likely the result of Cu^{2+} impurity moments, or rare-earth impurities, and corresponds to a molar fraction of $<5\%$, assuming a moment of $2\mu_B$. Due to the chemical similarity of the rare earths, we expect this impurity concentration will be of similar magnitude for the other compounds studied.

The magnetothermal behavior of $R\mathrm{CuO_2}$ for the non-Kramers ions R=Pr and Eu is described next. The susceptibilities of these compounds, shown in Fig. 2, do not display Curie-Weiss behavior in the measurement range of this study. Since the R=Eu compound has a $^7F_0$ ground state, the constant susceptibility observed at the lowest temperatures is due to Van Vleck paramagnetism. Assuming a J=1 singlet as the first excited level, the T=0 Van Vleck contribution yields 297 K for the energy of this level, as expected for Eu^{3+}. For R=Pr, even though the susceptibility is still evolving at 2 K, the $C(T)$

TABLE I. Lattice constants of $R\mathrm{CuO_2}$ rhombohedral space group $R\bar{3}m$.

	a (Å)	c (Å)	V (Å^3)
$\mathrm{LaCuO_2}$	3.833(2)	17.110(9)	217.7(3)
$\mathrm{PrCuO_2}$	3.747(2)	17.067(6)	207.5(3)
$\mathrm{NdCuO_2}$	3.714(2)	17.104(9)	204.3(3)
$\mathrm{SmCuO_2}$	3.660(1)	17.067(4)	198.0(2)
$\mathrm{EuCuO_2}$	3.633(1)	17.091(4)	195.4(2)
$\mathrm{Gd_{0.1}La_{0.9}CuO_2}$	3.806(2)	17.099(9)	214.5(3)
$\mathrm{Gd_{0.6}La_{0.4}CuO_2}$	3.683(3)	17.12(2)	211.5(4)
$\mathrm{Gd_{0.8}La_{0.2}CuO_2}$	3.640(2)	17.131(8)	196.6(3)

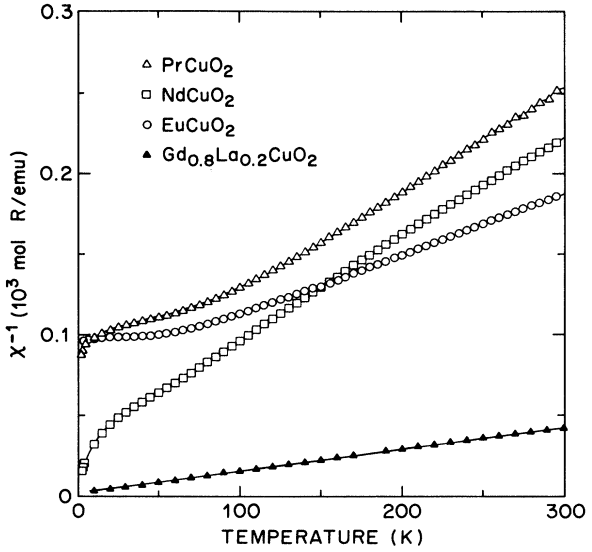

FIG. 2. Inverse susceptibility of several $RCuO_2$ compounds from 2 to 300 K. The rounded features below 50 K in the R=Pr and Nd data are most likely the result of crystal-field levels.

data, shown in the inset of Fig. 3, yield an entropy of $<0.1R$ ln2 between 0.1 and 2 K. Since no ordering anomaly is observed in $\chi(T>0)$, the small entropy reveals a singlet ground state, as might have been expected for the $^3H_4$ multiplet of Pr^{+}. The dominant contribution to $C(T)$ below 1 K has an inverse relationship with T and might be ascribed to either Cu or rare-earth impurities. From the above data, it can be concluded that the low-temperature thermodynamics is determined by single-ion properties for the non-Kramers ions.

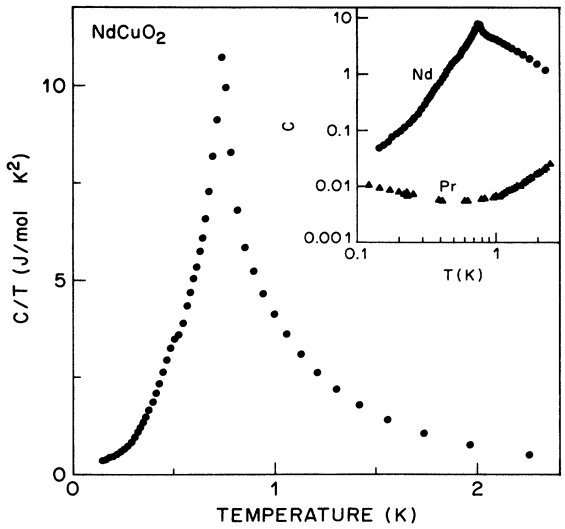

FIG. 3. Specific heat of $NdCuO_2$ and $PrCuO_2$ (shown in inset). The entropy involved in the ordering peak for $NdCuO_2$ is approximately 0.90 R ln2 at 2.25 K. The lack of an appreciable specific heat in $PrCuO_2$ is an indication of a singlet ground state.

In contrast to the non-Kramers ion, the Kramers-ion compounds do display cooperative behavior. For R=Nd, the ground-state multiplet is $^4I_{9/2}$. Consequently, the non-Curie-Weiss form of $\chi(T)$ above 10 K can be ascribed to the presence of crystal-field levels, most likely derived from the Γ_8 quartet.[20] Between 2 and 10 K, $\chi(T)$ displays Curie-Weiss behavior with $\Theta_{CW}=-4.4$ K. The dipole-dipole interaction is only of order 0.05 K, and so the main interaction is superexchange. An ordering anomaly is observed in $C(T)$ for the Nd compound at 0.72 K, as shown in Fig. 3. The entropy involved in the ordering process is approximately 0.90% R ln2 at 2.25 K, confirming the existence of only a Kramers doublet and no low-lying orbital states. In addition to the main peak is seen a small anomaly at 0.50 K, possibly due to 3D ordering among the Nd planes. We note the disparity between Θ_{CW} and T_c. The value $f=6.1$ indicates a moderate degree of frustration.

Finally, the compound corresponding to $R=La_{0.2}Gd_{0.8}$ is described. Gd^{3+} has a $^8S_{7/2}$ single-ion ground-state multiplet, and therefore crystal fields and the associated anisotropies play no role in the development of cooperative behavior. Unfortunately, the rhombohedral Delafossite-type structure is not stable for Gd, and so the fully concentrated compound could not be synthesized in bulk form. However, a substantial amount of $GdCuO_2$ can be dissolved in $LaCuO_2$, and it was possible to reach 80 at. % Gd concentration. (Traces of CuO and Gd_2O_3 impurity phases occurred for $La_{0.1}Gd_{0.9}CuO_2$). Initially it was thought that this value would not seriously degrade the cooperative behavior since the percolation threshold for the triangular lattice, 50%, was significantly smaller. In Fig. 4 is shown the low-T behavior of $\chi(T)$ and $C(T)$ for $La_{0.2}Gd_{0.8}CuO_2$. $\chi(T)$ obeys a Curie-Weiss law very well down to 10 K and yields $\Theta_{CW}=-12.5$ K and a moment of $7.912\mu_B$, the latter as expected for Gd^{3+} with a g factor of 1.994. The dipole-dipole interaction for this system is estimated to yield an ordering temperature of 2.5 K and superexchange again dominates the spin-spin interaction.

Surprisingly, in light of the ordering seen in the Nd analog, there is no distinct critical anomaly in $C(T)$, even though the magnetic concentration is well above the percolation threshold. Instead, only a broadened peak is observed at 1.8 K. The origin of this peak in AF short-range order is supported by the decrease in peak temperature with increasing magnetic field, shown in Fig. 4. In Fig. 5 are shown χ_{ac} data for $La_{0.2}Gd_{0.8}CuO_2$ at various driving field frequencies, below 1.5 K. The rounded shoulder observed in the 10-Hz data at 0.7 K is the only evidence for a cooperative transition down to 0.05 K in susceptibility measurements and we therefore identify this anomaly with the peak in $C(T)$. If the $C(T)$ peak corresponds to a disorder-broadened AF transition, then one would expect $\chi_{ac}(T)$ to peak at a higher temperature,[21] contrary to the observations. On the other hand,

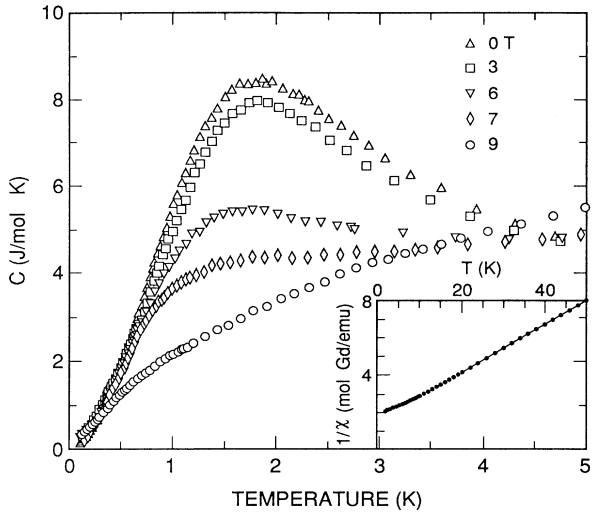

FIG. 4. Specific heat of $La_{0.2}Gd_{0.8}CuO_2$ vs temperature for several values of applied field. The decrease of the peak temperature with field indicates antiferromagnetic short-range order. The inset shows the inverse susceptibility for the same compound. The straight line is a least-squares fit, and yields $\Theta_{CW} = -12.5$ K and a moment of $7.912\mu_B$.

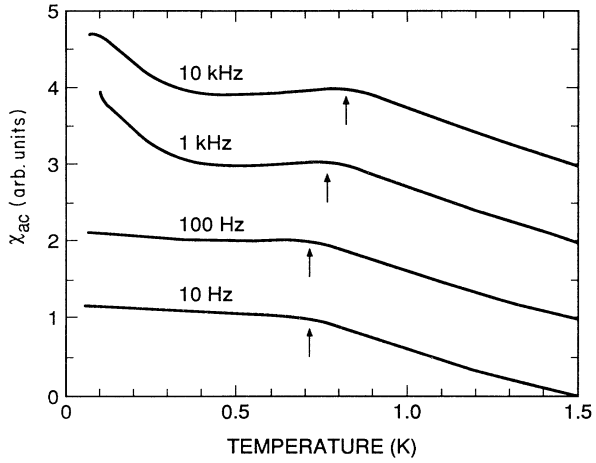

FIG. 5. ac susceptibility for $La_{0.2}Gd_{0.8}CuO_2$ vs temperature for different frequencies of driving field. The suspected spin-glass ordering anomalies are indicated by arrows.

both the order in which the peaks occur and the rounded nature of the $C(T)$ peak is consistent with a spin-glass transition. In support of this picture is the frequency dependence of $\chi_{ac}(T)$. Normally, for a Néel transition, one expects no shift in the peak temperature in the frequency range employed here. Spin-glass materials, however, exhibit relaxation effects over a broad range of frequencies, and are usually observable in the audio-frequency range. If the $\chi_{ac}(T)$ anomaly is actually an inhomogeneously broadened spin-glass peak, then the upward shift in peak temperature with increasing frequency is as expected. Therefore, given the above thermodynamic behavior and the known site disorder in the compound, we conclude that $La_{0.2}Gd_{0.8}CuO_2$ enters a spin-glass state at $T_g = 0.7$ K.

For $La_{0.2}Gd_{0.8}CuO_2$, $f = 17$, indicating, as for the Nd analog, a frustrated state. The spin-glass behavior in the weakly diluted Gd compound underscores the failure of percolation theory for highly frustrated systems. This has been noted before—for example, it is dramatically illustrated in dilution studies[22] of the B-site spinel compound $Zn(Cr,Ga)_2O_4$, for which $f = 25$. In this compound, Néel order is replaced by a spin-glass state at only 15% Ga concentration.

We conclude that in none of the studied compounds is a RVB-like state observed. For the Kramers systems, we infer Néel order for $R = Nd$, and spin-glass order for $R = La_{0.2}Gd_{0.8}$. However, the spin-glass state arises from atomic site disorder—in this case, it is not clear whether a RVB-like state would be stable anyway. The high degree of frustration found for the Gd compound suggests that the fully occupied system would be a good candidate for complete frustration. The large Gd spin, however, will make quantum effects negligible and thus the connection to RVB behavior tenuous.

Further investigation of this system will be subject to the availability of single crystals. The full occupied Gd compound might be stable if grown epitaxially. Of much interest will be the phase diagram for the Kramers systems in the H-T plane. The present investigation demonstrates, however the feasibility of addressing a range of frustration-related issues in a triangular-symmetry rare-earth magnet.

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[1](a) L. J. de Jongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974); (b) *Magnetic Properties of Layered Transition Metal Compounds*, edited by L. J. de Jongh (Kluwer, Boston, 1990).

[2]P. W. Anderson, Science **235**, 1196 (1987).

[3]P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).

[4]S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. Lett. **60**, 1057 (1988); J. D. Reger and A. P. Young, Phys. Rev. B **37**, 5978 (1988); P. Horsch and W. von der Linden, Z. Phys. B **72**, 181 (1988); R. R. P. Singh, Phys. Rev. B **39**, 9760 (1989).

[5]G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Kastner, Y. Hikada, M. Oda, M. Suzuki, and T. Murakami, Phys. Rev. Lett. **59**, 1613 (1987).

[6]For a general discussion of frustration in Ising systems, see R. Liebmann, *Statistical Mechanics of Periodic Frustrated Ising Systems* (Springer-Verlag, Heidelberg, 1986).

[7]G. Toulouse, Commun. Phys. **2**, 115 (1977); Phys. Today **42** (12), 97 (1989).
[8]K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[9]D. A. Huse and V. Elser, Phys. Rev. Lett. **60**, 2531 (1988).
[10]G. H. Wannier, Phys. Rev. **79**, 357 (1950); Phys. Rev. B **7**, 5017 (1973). See also R. M. F. Houtappel, Physica **16**, 425 (1950).
[11]R. B. Stinchcombe, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Leibowitz (Academic, London, 1983), Vol. 7.
[12]M. Steiner, J. Villain, and C. G. Windsor, Adv. Phys. **25**, 87 (1976).
[13]H. Kawamura and S. Miyashita, J. Phys. Soc. Jpn. **53**, 9 (1984).
[14]D. H. Lee, J. D. Joannopolous, J. W. Negele, and D. P. Landau, Phys. Rev. Lett. **52**, 433 (1984).
[15]H. Kawamura, J. Appl. Phys. **63**, 3086 (1988).
[16]For a short review, see H. Hirakawa and H. Ikeda in Ref. 1(b), p. 231.
[17]H. Hirakawa, H. Kadowaki, and K. Ubukoshi, J. Phys. Soc. Jpn. **52**, 1814 (1983); K. Takeda, K. Ubukoshi, T. Haseda, and K. Hirakawa, *ibid.* **53**, 1480 (1984).
[18]J. Doumerc, A. Wichainchai, A. Ammar, M. Pouchard, and P. Hagenmuller, Mater. Res. Bull. **21**, 745 (1986) on $CrCuO_2$; A. P. Ramirez, G. P. Espinosa, and A. S. Cooper, Phys. Rev. Lett. **64**, 2070 (1990) on $SrCr_8Ga_4O_{19}$; R. Plumier, M. Lecomte, and M. Sougi, J. Phys. (Paris) Lett. **38**, L149 (1977), and references cited therein, on $ZnCr_2O_4$.
[19]H. Haas and E. Kordes, Z. Kristallogr. **129**, 259 (1969).
[20]K. R. Lea, M. J. M. Leask, and W. P. Wolf, Phys. Chem. Solids **23**, 1381 (1962).
[21]M. E. Fisher, Philos. Mag. **7**, 1731 (1962).
[22]D. Fiorani, S. Viticoli, J. L. Dormann, J. L. Tholence, and A. P. Murani, Phys. Rev. B **30**, 2776 (1984).

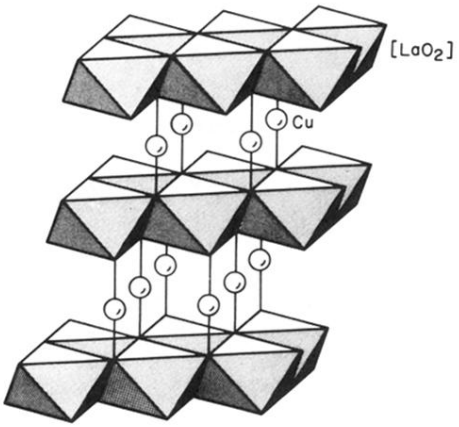

FIG. 1. View of the Delafossite-type structure for $R\mathrm{CuO}_2$. RO_6 octahedra and Cu atoms are depicted.