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Effect of sulfur on the superconductivity of $RBa_2Cu_3O_7$

I. Felner* and B. Barbara

Laboratoire L. Néel, 166X Grenoble, France

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The single-phase high- T_c superconductor $RBa_2Cu_3O_6S$, $R = Nd, Eu, Gd, Y, Er$, has been prepared and studied by x-ray diffraction and dc magnetometry. For Gd and Y the compounds with sulfur have a larger unit cell and yet have the same T_c . For $R = Eu, Nd$ substitution of one oxygen by sulfur suppresses T_c and causes the crystal structure to change from orthorhombic to tetragonal. $TbBa_2Cu_3O_{7-x}S_x$, $x = 0, 1$ systems crystallize in the perovskite-related cubic structure and are neither superconducting nor magnetically ordered down to 2 K. The sulfur oxidizes the Tb so that it is tetravalent.

In previous papers,^{1,2} it was shown that substitution of one oxygen in $YBa_2Cu_3O_7$ with sulfur ($YBa_2Cu_3O_6S$) does not change T_c , and the latter compound has even a sharper transition and its Meissner effect is almost complete. The fact that T_c is not affected is consistent with reported observations about the lack of strong [Bardeen-Cooper-Schrieffer (BCS) type] oxygen isotope effect.³ An exciting challenge is to understand the influence of sulfur on other high- T_c $RBa_2Cu_3O_7$ compounds. In this paper we report the crystal structure and magnetic characteristics of some $RBa_2Cu_3O_7$ ($R = Nd, Eu, Gd, Tb$, and Er) and compare them to $RBa_2Cu_3O_6S$ compounds, which have been prepared for the first time. In the case of $R = Nd$, we succeeded in replacing two oxygen atoms by sulfur. No change in T_c occurs when one oxygen is substituted for $R = Gd$ and both samples are orthorhombic; $GdBa_2Cu_3O_6S$, however, has a larger unit cell than $GdBa_2Cu_3O_7$. On the other hand, for $R = Nd$ and Eu , T_c decreases with increasing sulfur content and detailed x-ray analysis shows that the compounds $RBa_2Cu_3O_xS_{7-x}$ crystallize in the tetragonal (II) type structure. For $R = Tb$ neither compound is superconducting or magnetically ordered down to 1.6 K, and both crystallize in a cubic structure which is also related to a perovskite type. The oxidation state of Tb is +3 in $TbBa_2Cu_3O_7$ and +4 in $TbBa_2Cu_3O_6S$.

Samples of nominal composition $RBa_2Cu_3O_7$ and $RBa_2Cu_3O_6S$ ($R = Nd, Eu, Gd, Tb$, and Er) were prepared by thoroughly mixing appropriate amounts of R_2O_3 (Tb_2O_3), $BaCO_3$, CuO , and CuS powders. The mixed powders were pressed and packed into alumina crucibles and heated $950^\circ C$ in air for 12–15 h. The mixtures were then cooled to ambient temperatures ground, mixed and pressed into pellets, sintered again in $950^\circ C$ for 3 h and then cooled to $650^\circ C$ in flowing O_2 for several hours, and cooled slowly to $200^\circ C$ in O_2 before removal from the furnace. R -based compounds with and without sulfur were prepared at the same time and therefore under the same conditions. Samples were examined by x-ray powder diffraction using $Co K\alpha$ radiation. The diffraction patterns show that all the observed lines can be indexed as a single phase with crystal structure and lattice parameters listed in Table I. The dc susceptibility (M/H) measurements were carried out by a superconducting quan-

tum interference device (SQUID) magnetometer in various magnetic fields $4 Oe < H < 50 kOe$ as a function of temperature in the range of 1.5–300 K. The curves shown in Figs. 1–3 were obtained by field cooling the samples from above T_c . Resistance measurement was made with a standard four-probe technique on a rectangular sample cut from the sintered pellet.

X-ray powder diffraction shows that the compounds of nominal composition $GdBa_2Cu_3O_{7-x}S_x$, where $x = 0, 1$, are single phase, and crystallize in the orthorhombic structure. From the lattice parameters given in Table I, one sees a definite expansion for $x = 1$, which indicates that the bigger sulfur atoms really replace oxygen. Both compounds were examined by scanning electron microscope. Their compositions were found to be uniform from grain to grain, and the nominal compositions were confirmed. Assuming that ions enter the lattice substitutionally at the oxygen sites, it is not clear yet whether the replacement occurs preferentially in the Cu-O chains or the S ions are distributed at random among all the oxygen sites. X-ray intensity measurements show clearly an increase in the (005) reflection peak for the compound with sulfur,⁴ and the detailed structure is now under investigation.

Figure 1 presents the susceptibility curves as a function of temperature for $GdBa_2Cu_3O_7$ and $GdBa_2Cu_3O_6S$. The curves were measured when cooling the samples from well above T_c to low temperatures. Qualitatively, the two samples exhibit similar magnetic properties below and above T_c . The most exciting fact is that sulfur does not affect T_c , which is 92 K for $x = 0, 1$. It should be mentioned that the same phenomenon is observed in $YBa_2Cu_3O_{7-x}S_x$;^{1,2} however, here the transition for $GdBa_2Cu_3O_6S$ is not sharp and the Meissner effect value is even smaller than that of $GdBe_2Cu_3O_7$. The magnetization field dependence at 3 K is exhibited in the inset of Fig. 1. For both compounds the negative magnetization in the perfect diamagnetic state is linear with the applied field and passes at H_{c1} to the mixed state. H_{c1} for $GdBa_2Cu_3O_6S$ is higher than that for $GdBa_2Cu_3O_7$ (Table I) although the volume susceptibility is only 29% and 35% of $-1/4\pi$, respectively.

We turn now to the results of $GdBa_2Cu_3O_{7-x}S_x$ above T_c . Since the Gd ions are expected to interact strongly, we analyze χ for $T > T_c$ using the Curie-Weiss relation:

TABLE I. Lattice parameters and superconducting and magnetic data for $RBa_2Cu_3O_{7-x}S_x$ compounds.

Compound	Crystal structure	Lattice parameters				Superconducting data			Magnetic data			
		a (Å)	b (Å)	c (Å)	V (Å ³)	T_c (K)	H_{c1} (Oe)	Meissner effect (%)	C (emu/mole)	Θ (K)	P_{eff}^{obs} (μ_B)	P_{eff}^{calc} (μ_B)
NdBa ₂ Cu ₃ O ₇	ortho	3.873	3.906	11.73	177.5	88			1.56	-36	3.53	3.62
NdBa ₂ Cu ₃ O ₆ S	tetra II	3.879		11.69	177.5	69			1.60	-40	3.58	
NdBa ₂ Cu ₃ O ₅ S ₂	tetra II	3.897		11.69	177.5	56			1.65	-57	3.64	
EuBa ₂ Cu ₃ O ₇	ortho	3.821	3.884	11.61	172.3	92	350	65	1.16	-12	3.05	
EuBa ₂ Cu ₃ O ₆ S	tetra II	3.884		11.65	175.7	85						
GdBa ₂ Cu ₃ O ₇	ortho	3.844	3.897	11.70	175.2	92	450	35	8.0	0	8.03	7.94
GdBa ₂ Cu ₃ O ₆ S	ortho	3.887	3.911	11.72	178.2	92	700	29	8.3	0	8.17	
GdBa ₂ Cu ₃ O ₆ S ^a	tetra I	3.899		11.85	180.1				8.8	-12	8.33	
TbBa ₂ Cu ₃ O ₇	cubic	8.572			629.9				11.8	-50	9.70	9.72
TbBa ₂ Cu ₃ O ₇ ^a	cubic	8.572			629.9				11.8	-70	9.60	
TbBa ₂ Cu ₃ O ₆ S ^b	cubic	8.572			629.9				8.5	-40	8.23	

^aQuenched from 800 °C.^bContains about 5% of BaSO₄.

$\chi = \chi_0 + C/(T - \Theta)$ where Θ is the Curie-Weiss temperature. In this case, χ_0 , the temperature-independent susceptibility is extremely small (on the order of $1-2 \times 10^{-6}$ emu/gOe) relative to the temperature-dependent Gd paramagnetism and can be neglected. The magnetic data listed in Table I were obtained by plotting $1/(\chi - \chi_0)$ vs T . The straight lines yield $\Theta = 0$ in good agreement with the determination in Refs. 5 and 6. The measured effective moment P_{eff} values, agree well to $7.94\mu_B$ expected for

ground state of Gd^{3+} .

The tetragonal (I) phase for $GdBa_2Cu_3O_6S$ was obtained by heating the sample to 800 °C for 2 h and quenching it into liquid nitrogen. The c lattice constant expands and the compound is not superconducting down to 2 K. It is evident that the effective magnetic moments for both orthorhombic and tetragonal phase are virtually the same, since the quenching procedure affects only the oxygen concentration and leaves the remainder of the lattice unchanged.

The system $ErBa_2Cu_3O_{7-x}S_x$, $x=0,1$ was also prepared, but the x-ray pattern for $ErBa_2Cu_3O_6S$ showed

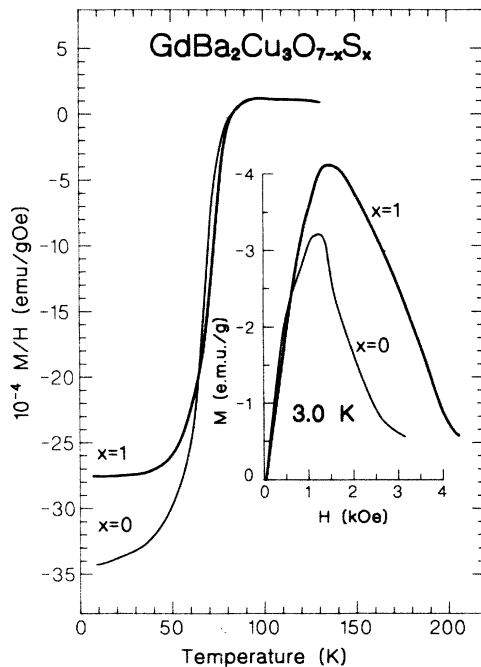


FIG. 1. Magnetic susceptibility vs temperature curves at $H=7$ Oe, for $GdBa_2Cu_3O_{7-x}S_x$ where $x=0$ and 1, measured by SQUID magnetometer. The inset shows the field dependence of the magnetization at 3.0 K. The deviation from linearity is defined as H_{c1} .

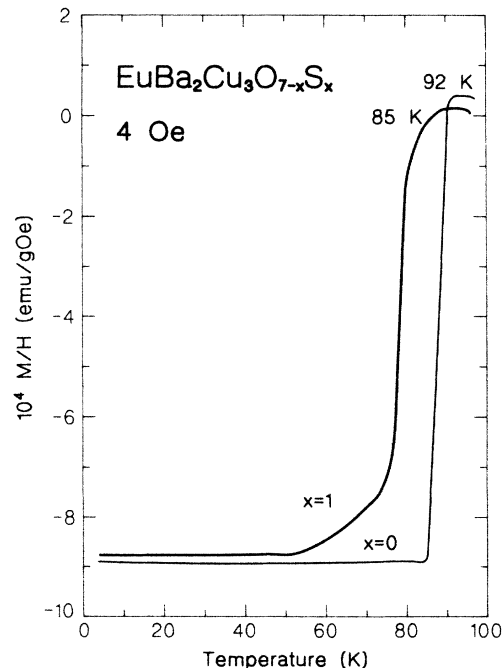


FIG. 2. Magnetic susceptibility vs temperature curves at 4 Oe for $EuBa_2Cu_3O_{7-x}S_x$ where $x=0$ and 1.

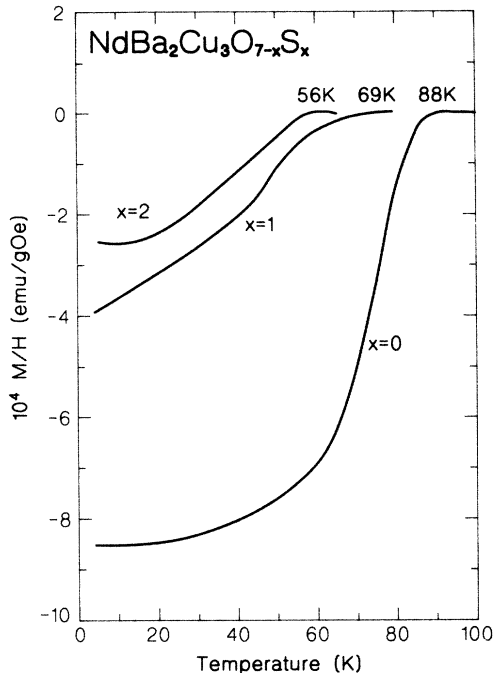


FIG. 3. Magnetic susceptibility vs temperature curves at 7 Oe for $\text{NdBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$ $x=0, 1$, and 2.

that beside the main peaks corresponding to the orthorhombic phase, there is an additional phase that accounts for at least a third of the intensity. T_c is the same for both samples which means that sulfur does not affect T_c . However it is very likely that in this case the sulfur atoms did not enter into the compound since Er has a small unit-cell volume.

In contrast to $\text{RBa}_2\text{Cu}_3\text{O}_{6-x}\text{S}_x$, $R=\text{Gd}, \text{Y}$, systems, substitution of oxygen by sulfur suppresses T_c where $R=\text{Eu}$ and Nd . Figures 2 and 3 represent the susceptibility curves for both systems. The decrease in T_c is smaller in $\text{EuBa}_2\text{Cu}_3\text{O}_6\text{S}$ than in $\text{NdBa}_2\text{Cu}_3\text{O}_6\text{S}$. In $\text{NdBa}_2\text{Cu}_3\text{O}_5\text{S}_2$ a small amount of BaSO_4 is observed in the x-ray pattern and the exact proportion of sulfur is, therefore, less than 2. In addition to the reducing of T_c , the sulfur smears the transition below T_c .

It is interesting to see that the paramagnetic effective moment in the normal region and the Curie-Weiss temperature Θ do not change when oxygen is replaced by sulfur and the negative Θ value indicates that within these compounds Nd ions interact antiferromagnetically. Our values are similar to data in Refs. 5 and 7. Note the agreement between the value obtained experimentally and $3.64\mu_B$ the theoretical value for Nd^{3+} . The P_{eff} value obtained for $\text{EuBa}_2\text{Cu}_3\text{O}_7$ is typical to Eu^{3+} ion at high temperatures if contributions from excited multiplets are included. The susceptibility of $\text{EuBa}_2\text{Cu}_3\text{O}_6\text{S}$ is particularly unusual. The reciprocal susceptibility cannot be fitted with a Curie-Weiss law, and we have considered the possibility that the Eu ions may exhibit a mixed valent state. This, however, seems unlikely, due to the fact that only the Eu^{3+} states were found in preliminary Eu^{151} Mössbauer measurements. The isomer shift for both

$\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$, $x=0, 1$ compounds at room temperature is 0.75 mm/sec with respect to the $^{151}\text{SmF}_3$ source which is typical of Eu^{3+} found in many oxides. There is no change in the electric-quadrupole interactions in these compounds. The most likely cause for the anomalous susceptibility of $\text{EuBa}_2\text{Cu}_3\text{O}_6\text{S}$ is the strong influence of the excited multiplets ($J=1, 2$) of Eu^{3+} lying only a few hundred degrees above the ground state multiplet $J=0$. The qualitative difference observed in the susceptibility with and without sulfur suggests that the chemical bonding of Eu^{3+} is modified by the presence of sulfur in a way such that the separation between $J=0$ and $J=1$ is lowered.

We turn now to the crystal structure of $\text{RBa}_2\text{Cu}_3\text{O}_6\text{S}$, $R=\text{Nd}$ and Eu . The x-ray patterns of $\text{EuBa}_2\text{Cu}_3\text{O}_7$ and $\text{EuBa}_2\text{Cu}_3\text{O}_6\text{S}$ are shown in Fig. 4. One definitely sees the shift to lower 2θ values of the peaks belonging to $\text{EuBa}_2\text{Cu}_3\text{O}_6\text{S}$ which indicate a larger unit-cell volume. Moreover, the doublets (020.006) (200) or (213) (123) which are typical of the orthorhombic cell coincide with singlets, and the patterns can be indexed on the basis of the tetragonal unit cell. On the other hand, in $\text{NdBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$ where $x=1, 2$ the main peaks corresponding to this tetragonal structure have the same 2θ values as the orthorhombic cell of $\text{NdBa}_2\text{Cu}_3\text{O}_7$, which means that the unit-cell volume of both structures is essentially the same. Stated differently, the unit-cell volume of $\text{NdBa}_2\text{Cu}_3\text{O}_7$ is large enough to accommodate the big sulfur atoms without any expansion.

At this point we consider the difference between the two tetragonal structures mentioned above. In the nonsuperconducting tetragonal phase (I) obtained by quenching the sample from high temperatures the concentration of oxygen is 6.3, whereas in the superconducting orthorhombic phase it is about 7. The extra oxygens occupy the sites on the basal plane along the b lattice axis which is stretched by about 1.5% compared to the a axis resulting in the orthorhombic deformation. In the orthorhombic cell the ratio of the lattice parameters $c/b=3$. However, the c value in the tetragonal (I) increases by about 1% ($c/a > 3$), and this elongation along the c axis is thought

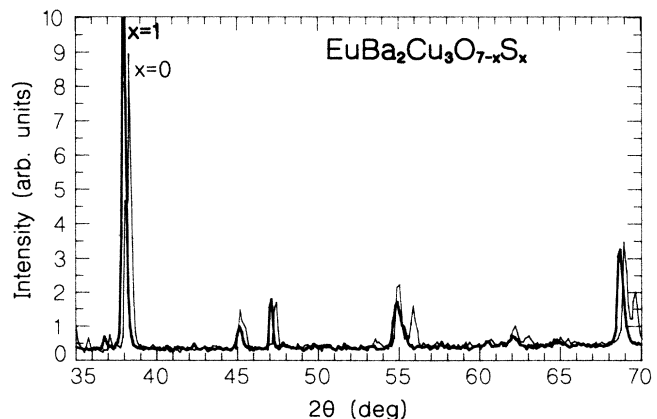


FIG. 4. X-ray diffraction patterns of the orthorhombic $\text{EuBa}_2\text{Cu}_3\text{O}_7$ and the tetragonal (II) phase of $\text{EuBa}_2\text{Cu}_3\text{O}_6\text{S}$ (bold line). The spectra were taken using 1.79 Å Co radiation. Note the shift of the main peaks to lower 2θ values.

to be the result of an increase in the number of oxygen vacancies.

The superconducting tetragonal phase (II) is the result of impurities doped (like Fe) in copper sites⁸ or oxygen substituted by sulfur (Table I). Both substitutions cause the transition from an ordered orthorhombic cell into a disordered phase which is observed to be tetragonal by the x-ray diffraction method. The concentration of oxygen is quite the same as that of the orthorhombic structure, and the c/a ratio remains equal to 3. In other words the tetragonal (II) phase has indeed an orthorhombic local symmetry with, accidentally, the same a and b lattice constants.

The $\text{TbBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$ system behaves completely differently from the superconducting compounds mentioned above. $\text{TbBa}_2\text{Cu}_3\text{O}_7$ is not superconducting even though its neighboring compounds with Gd and Dy are. Perhaps this is because Tb can have two oxidation states (3^+ and 4^+) as indicated by its starting oxide Tb_4O_7 . To prove this assumption we prepared the nominal composition of the system $\text{TbBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$, $x=0,1$. It appears that neither compound is superconducting or magnetically ordered down to 1.6 K. $\text{TbBa}_2\text{Cu}_3\text{O}_7$ shows semiconducting behavior and the resistivity increases by 4 orders of magnitude as the temperature is lowered from 300 to 40 K.

The x-ray pattern definitely shows the existence of a fcc cubic structure which does not change by quenching the sample from 800°C or by replacing oxygen with sulfur. About 3% of additional lines belonging to CuO are also seen in all the diffractograms. The interplanar spacing and the relative intensities are (4.285, 3.027, 2.137, 1.747, 1.512 Å) and (1, 100, 36, 47, 40), respectively. These values are very similar to $\text{Ba}_3\text{MnU}_2\text{O}_9$ (Ref. 9) which crystallizes in a cubic structure which is related to that of a perovskite. It means that both Tb and Ba ions reside in one of the crystallographic sites of the reduced ABO_3 perovskite structure, but these are ordered in such a manner that the unit cell must be doubled giving a larger lattice constant 8.572 Å.¹⁰ This value is 10% larger than twice the average dimension 3.86 Å of the basal a axis in either the orthorhombic or the tetragonal structure. The detailed structure and the oxygen content are now under investigation.

The paramagnetic Curie-Weiss temperatures and the Curie constants (Table I), obtained by fitting the inverse

susceptibility, were measured at 10 kOe in a temperature range of 4–300 K, with the Curie-Weiss relation mentioned above. The high negative Θ values indicate that within this structure the Tb ions interact antiferromagnetically. The experimental P_{eff} for $\text{TbBa}_2\text{Cu}_3\text{O}_7$, quenched and unquenched, are very close to $9.72\mu_B$ expected for the ground state of Tb^{3+} , according to the Hund's rules. Surprisingly, for the compounds which contain sulfur P_{eff} is $8.2\mu_B$, very similar to values obtained for Gd compounds, which indicate that both Gd and Tb have the same electronic configurations. Our starting source for sulfur was CuS which decomposes to elements Cu and S at about 220°C. It happens that the S^0 in order to replace O^{2-} acts as an oxidizing agent and oxidizes Tb to its tetravalent state. The larger size of S is compensated by the reduce size of Tb^{4+} , and the lattice parameter does not change.

To summarize, we have shown that the replacement of oxygen by sulfur atoms in the heavy superconductors $\text{RBa}_2\text{Cu}_3\text{O}_7$, $R=\text{Gd}, \text{Y}(\text{Er})$ does not affect the superconducting properties of the materials. The crystal structure expands but stays orthorhombic. The crystallographic positions of the sulfur atoms are now under investigation. In contrast we have found that for the light superconductors $R=(\text{Eu}, \text{Nd})$ with larger unit cell volumes, T_c is suppressed by this substitution, which is followed by a change of the crystal structure from orthorhombic to tetragonal (II). Is there a connection between the reduction in T_c and the metamorphosis? We found that for $R=\text{Gd}$ the compound with the sulfur has a smaller Meissner effect but a larger critical field H_{c1} while the paramagnetic properties above T_c do not change. The larger the crystallographic parameters of the host ($2S$ in Nd, $1S$ in Eu, and no S in Er^{3+}), the more easily the sulfur enters the structure. $\text{TbBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$, $x=0,1$ systems crystallize in a cubic structure which is related to the perovskite type. Quenching the samples does not affect the crystal structure or the magnetic properties. None of these systems is superconducting or magnetically ordered down to 1.6 K. Tb is trivalent for $x=0$ and tetravalent for $x=1$.

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*Permanent address: Racah Institute of Physics, Hebrew University, Jerusalem, Israel.

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