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Physics Abstracts

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The crystal structure of $\text{RESr}_2\text{GaCu}_2\text{O}_7$

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Abstract. — The crystal structure of $\text{RESr}_2\text{GaCu}_2\text{O}_7$ (with RE=Er...La and Y) has been studied by powder neutron, powder X-ray and single crystal X-ray diffraction. These compounds crystallize in space group $\text{Ima}2$ with approximate lattice parameters $a \approx 22.8\text{Å} \approx 2 \cdot c$ (1-2-3), $b \approx 5.5\text{Å} \approx \sqrt{2} \cdot b$ (1-2-3) and $c \approx 5.4\text{Å} \approx \sqrt{2} \cdot a$ (1-2-3) and 4 formula units per cell. Like the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ ("1-2-3") the structure contains double layers of Cu-O₅-pyramids separated by Y or trivalent rare earth ions. The Cu-O₄ square planar chains of 1-2-3, however, are replaced by Ga-O₄ tetrahedral chains running along the diagonal of the basal plane of the 1-2-3 subcell. The role of Ba to fill the large voids in 1-2-3 is played by Sr in these compounds. The structure forms with Y and all trivalent rare earth ions from Er through La with the exception of Ce. The oxygen stoichiometry is fixed to O₇ and the compounds are semiconducting. They can be p-doped by partially replacing RE by divalent earth alkali ions, thus reducing the resistivity drastically. However, despite their strong similarity to 1-2-3, particularly with respect to the CuO₅-pyramidal bilayers, combined with the possibility of p-doping, all attempts to make these compounds metallic or even superconducting have failed so far.

1. Introduction.

The relation between crystal structures and superconducting properties of high- T_c superconductors, and particularly of the so-called 1-2-3 family of compounds (with $\text{YBa}_2\text{Cu}_3\text{O}_7$ as their protagonist) has been the subject of extensive research during the last 4 years since the discovery [1] and first structural characterization [2] of this class of compounds and has made $\text{YBa}_2\text{Cu}_3\text{O}_7$ probably one of the most intensely studied (but not necessarily one of the best understood) complex inorganic substances.

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In order to establish knowledge about structural prerequisites for high- T_c superconductivity and to identify and understand the various structural influences on T_c , a number of different approaches have been used. The basic idea is to modify the structure in some way and correlate these modifications with changes of the properties of the substance and of superconductivity in particular. Besides the more "physical" ways to perform a structural modification like, for instance, changing sample temperature or applying external pressure, there are several "chemical" ways to accomplish this, for instance by changing the oxygen stoichiometry, replacing oxygen by fluorine, replacing Y by rare earth ions or alkaline earth ions and also by partially replacing Cu by some other small cation like transition metal or group III cations. Each of these interventions into the structure has characteristic effects on both the crystal structure and the superconducting properties [3,4]. Replacing Y by rare earths, for instance, changes markedly some of the nearest neighbour distances (RE-O) but leaves others almost unaltered (in-plane Cu-O) and has virtually no effect on T_c . This has, in a very early stage, been taken as an indication that the Cu-O planes are most important for superconductivity in these compounds. This assumption was further supported by the observation that even small amounts of dopants on the Cu sites reduce the superconducting transition temperature T_c drastically. In some cases this doping on the Cu site is accompanied by structural changes as for instance in the case of Fe [5-7] and Co [8,9], where the apparent symmetry of the crystals changes from orthorhombic to tetragonal and the microstructure is drastically altered, however, without obvious correlations to superconducting properties. In other cases like Zn and Ni there are only subtle structural changes although T_c decreases even more drastically [10,11]. Obviously, the effects of changes of the crystal structure and of predominantly electronic modifications upon doping on the Cu-site(s) are intimately mixed and the separation of both is an important problem yet to be solved.

From a diffractionist's point of view, modification of the crystal structure by partial chemical substitution carries along with it a principle complication: Due to the structural disorder invariably introduced by partial replacement, quite a bit of information on the local environment of the atoms is lost because diffraction, as a method which probes long range ordered structural elements, yields averaged atom positions and averaged bondlengths only. In cases where the distribution of these quantities is broad, the averaged values may be of little use, particularly if they are intended to be correlated with "short range phenomena" like superconductivity. This is why in cases where disorder is a problem, a situation which is typical for high- T_c superconductors (which, by their own nature, are hardly ever stoichiometric) the "complementary" local structural probes like electron microscopy, EXAFS or Mössbauer spectroscopy, although less "quantitative" than diffraction, become extremely valuable tools for structural analysis.

The situation changes in favour of diffraction methods if a site (here the former Cu(1) chain site) is fully and exclusively occupied by some other species. In this way one obtains stoichiometric compounds instead of partially substituted (and disordered) ones. Many groups have claimed the existence of such 1-2-3 derivatives, however, we are aware of only three cases where a complete substitution for Cu(1) has been accomplished and has been proven by decent measurements. They are the closely related compounds $\text{LaBa}_2\text{TaCu}_2\text{O}_8$ [12,13] and $\text{LaBa}_2\text{NbCu}_2\text{O}_8$ [14], both with Ta-O₆ or Nb-O₆ octahedra replacing the Cu-O₄ squares and a Pd substituted 1-2-3 with Pd exclusively occupying the square planar coordinated former Cu(1)-(chain-) site [15]. The structure of $\text{YBa}_2\text{WCu}_2\text{O}_{9-\delta}$ [16] on the other hand is a cation-ordered variant of the cubic perovskite structure and is therefore not considered to be a derivative of 1-2-3, although the chemical formula seems to suggest this. In a broader sense the oxygen ordered phases of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and the "stacking variants" $\text{YBa}_2\text{Cu}_4\text{O}_8$ [17] and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ [18] with double chains of Cu-O₄ squares also belong to this group of "fully substituted" 1-2-3 derivatives. The class of compounds we are going to report on in this paper has Ga-O₄ tetrahedral chains substituted for the Cu-O₄ square planar chains. Due to the topological problem of fitting tetrahedra into a network of (incomplete)

Cu-O₆ octahedra the atom positions and also the unit cell dimensions and the symmetry are more drastically changed than in most of the cases mentioned above.

2. Preparation.

Single phase samples of $\text{RESr}_2\text{GaCu}_2\text{O}_7$ can be prepared by the following procedure: RE_2O_3 (Y_2O_3 , Tb_4O_7 , Pr_6O_{11}), SrCO_3 , Ga_2O_3 and CuO are intimately mixed in a ball mill, the mixture is calcinated at 900°C in air for 10 hours, homogenized by ball milling, pressed into pellets, fired at 950°C in air for 20 hours, ball milled and pelletized again and then annealed at 960°C for another 20 h in air followed by unregulated furnace cooling to room temperature within about 6 hours. DSC/TG analysis (see Fig. 1) performed in air on two representative samples, one with a small trivalent cation (Y) and the other with a large one (Nd) show no oxygen loss or uptake up to 1080°C and 1130°C , respectively. Above these temperatures a decomposition reaction occurs accompanied by a pronounced weight loss which is only partially reversible. Most probably at least part of the Cu^{2+} in the sample is being reduced to Cu^{1+} upon decomposition, leading to the evolution of oxygen and a corresponding weight loss. The decomposition is furthermore evidenced by the observation of transparent needles of Ga_2O_3 which are extruded from the surface of the pellets after prolonged heat treatment at temperatures above the decomposition temperature. We have no evidence for considerable amounts of a liquid phase being produced during this reaction. The Y-compound exhibits an additional endothermic peak at about 1000°C which occurs reversibly upon cooling provided the sample has not been heated above the decomposition temperature. It shows a hysteresis of about 20°C indicating that it is of first order. This peak could well be due to a structural phase transition, the nature of which is yet to be investigated. The preparation conditions given above apply to all rare earths from La through Er with the exception of the Ce compound which up to now could not be prepared in single phase form. Notably, $\text{TbSr}_2\text{GaCu}_2\text{O}_7$ forms the same structure whereas $\text{TbBa}_2\text{Cu}_3\text{O}_7$ does not crystallize in the 1-2-3 structure but in an ordered cubic perovskite variant [19]. As the DSC/TG results show, the stability of the compounds against thermal decomposition increases with increasing rare earth ionic radius. Samples with rare earth ions smaller than Er were not strictly single phase but the majority of the X-ray powder lines were still those of the title compound. Also, for the two largest RE-ions La and Pr, weak lines of an unknown phase appear. We believe that this is due to a tendency towards disordering of RE and Sr over the two sites available in the structure, accompanied by slight changes of stoichiometry as will be shown below.

The typical grain size of the crystallites growing during preparation by solid state reaction is very small, even after extended periods of heat treatment just below the decomposition temperature. It is therefore not practicable to grow by this method single crystals which are large enough even for single crystal X-ray studies. In only one case ($\text{YSr}_2\text{GaCu}_2\text{O}_7$) we were able to obtain a crystal of about $10\ \mu\text{m}$ in diameter by deliberately heating above the decomposition temperature for a short time. This crystal was used for the single crystal X-ray measurements (see below). Attempts to grow crystals of the title compound from various fluxes including "self-flux" have failed so far or have led to disordered variants of these compounds.

3. Structure determination and refinement.

The structure was initially determined from X-ray powder data of the Y-compound. Indexing of the pattern [20] yielded a monoclinic cell, very similar to "ordinary" 1-2-3 with $a = 3.846(1)\ \text{\AA}$, $b = 11.401(2)\ \text{\AA}$, $c = 3.846(1)\ \text{\AA}$, $\beta = 90.95(2)^\circ$ and possible space group P1m1 . Ri-

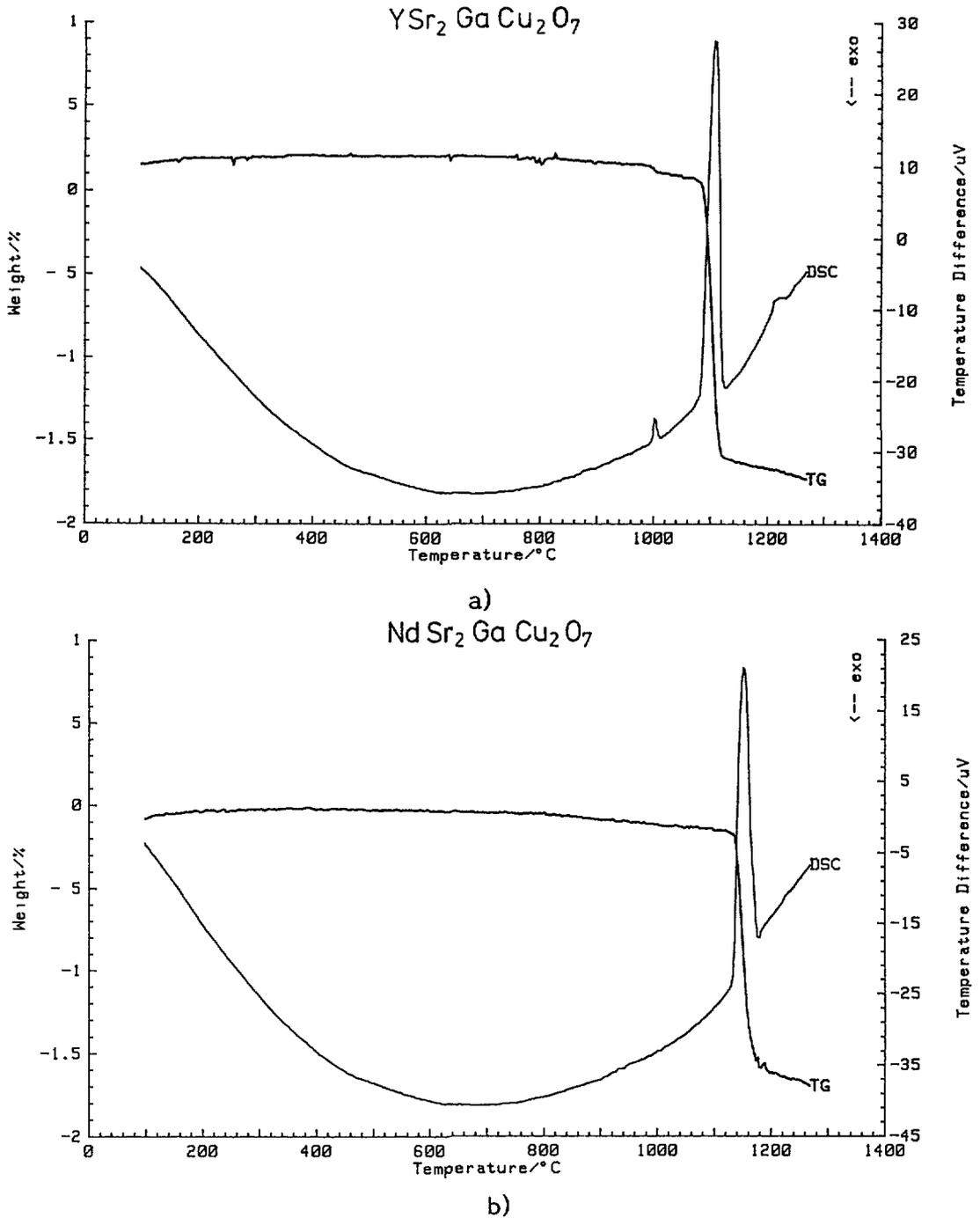


Fig. 1. — DSC/TG curves for a) $\text{YSr}_2\text{GaCu}_2\text{O}_7$, b) $\text{NdSr}_2\text{GaCu}_2\text{O}_7$.

etveld refinement using 1-2-3 coordinates as a starting set of parameters gave reasonable agreement factors but left some weak low angle reflections unaccounted for. Also, inspection of the

Table I. — Diffraction measurements, experimental details.

	Powder neutron diffraction	Powder X-ray diffraction	Single crystal X-ray diffraction
Samples	$\text{YSr}_2\text{GaCu}_2\text{O}_7$, $\text{NdSr}_2\text{GaCu}_2\text{O}_7$,	$\text{RESr}_2\text{GaCu}_2\text{O}_7$ RE: La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er; Y	$\text{YSr}_2\text{GaCu}_2\text{O}_7$
Space group	Ima2 (no. 46)	Ima2	Ima2
Sample mounting	Vanadium can, 12 mm diameter granulated pellets 6-10 g each	Li-borate glass capillary, 0.1 mm diameter, coated on the outside with sample powder (≈ 0.5 mg) (+ silicone grease). Absorption coefficient of the material: $\mu \approx$ 400-1000 cm^{-1} , depending on RE	single crystals ≈ 10 μm diameter
Temperature	6 K, 247 K	Room temperature	Room temperature
Atmosphere	Air	Air	Air
Equipment	D1A/ILL $\lambda = 1.9090(5)$ \AA $2\theta = 5^\circ - 150^\circ$, step 0.05° $\sin\theta/\lambda \leq 0.51$ ILL-cryostat type "orange"	STOE-powder diffractometer Debye-Scherrer geometry Monochromator: Ge(111) $\lambda = 1.54056$ \AA (CuK α_1) $2\theta = 10^\circ - 130^\circ$, step 0.02° $\sin\theta/\lambda \leq 0.59$ Position sensitive detector	STOE-4-circle diffractometer Monochromator: Graphite $\lambda = 0.71073$ \AA (MoK α) $2\theta \leq 75^\circ$, $\sin\theta/\lambda \leq 0.86$ $\pm h, \pm k, \pm l$ 584 independent reflections with $I > 2.5\sigma$ Internal R-value 8.5%
Data evaluation	Rietveld line-profile refinement [21] Profile function: Pearson VII	Rietveld line profile refinement Profile function: Pearson VII	Numerical absorption correction. Absorption coefficient $\mu = 340$ cm^{-1} Isotropic extinction correction Full matrix least squares Scattering factors for Y^{3+} , Sr^{2+} , Cu^{2+} , Ga^{3+} , O

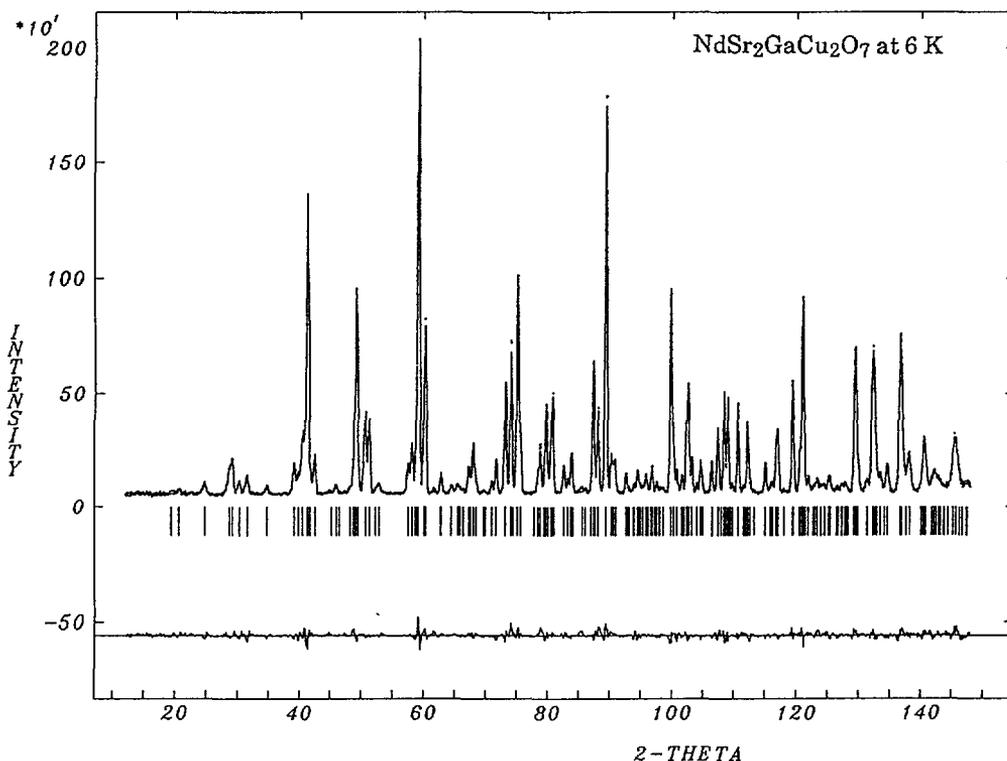
Fig. 2. — Powder neutron diffraction pattern of $\text{NdSr}_2\text{GaCu}_2\text{O}_7$ at 6 K.

Table II. — *Structural parameters.*

Sample method	YSr ₂ GaCu ₂ O ₇ ; 6 K powder neutron	YSr ₂ GaCu ₂ O ₇ , r.t. powder X-ray	YSr ₂ GaCu ₂ O ₇ , r.t. single crystal X-ray	NdSr ₂ GaCu ₂ O ₇ , 8 K powder neutron	NdSr ₂ GaCu ₂ O ₇ ; 247 K powder neutron	NdSr ₂ GaCu ₂ O ₇ , r.t. powder X-ray
a [Å]	22.7727(3)	22.8014(5)	22.793(7)	22.8874(3)	22.9245(3)	22.9201(6)
b [Å]	5.4767(1)	5.4819(1)	5.484(2)	5.5382(1)	5.5452(1)	5.5438(1)
c [Å]	5.3891(1)	5.3936(1)	5.396(2)	5.4360(1)	5.4439(1)	5.4408(1)
RE.						
x	0.5	0.5	0.5	0.5	0.5	0.5
y	0.0	0.0	0.0	0.0	0.0	0.0
z	0.0	0.0	0.0	0.0	0.0	0.0
N	1.0	1.0	1.0	1.0	1.0	1.0
B [Å ²]	0.87(6)	0.5	0.50(6)	0.88(8)	0.93(8)	0.5
Sr						
x	0.3496(1)	0.3495(2)	0.3493(2)	0.3489(1)	0.3488(1)	0.3488(3)
y	0.0137(3)	0.013(1)	0.0163(3)	0.0135(4)	0.0140(4)	0.011(2)
z	0.0013(7)	0.005(3)	-0.001(8)	0.0	0.0	0.0
N	0.976(7)	1.0	1.0	0.99(1)	0.99(1)	1.0
B [Å ²]	0.77(4)	0.7	0.69(5)	0.83(6)	0.96(6)	0.7
Cu						
x	0.4269(1)	0.4274(4)	0.4269(1)	0.4234(1)	0.4234(1)	0.4246(6)
y	-0.0003(3)	0.0	0.0005(5)	-0.0013(4)	-0.0007(4)	0.0
z	0.4984(7)	0.5	0.501(1)	0.4984(9)	0.4982(9)	0.5
N	1.0	1.0	0.992(9)	1.0	1.0	1.0
B [Å ²]	0.91(3)	0.5	0.51(6)	0.91(4)	0.88(4)	0.5
Ga						
x	0.75	0.75	0.75	0.75	0.75	0.75
y	0.4296(3)	0.435(2)	0.4309(6)	0.4307(4)	0.4308(5)	0.438(3)
z	0.0410(8)	0.038(3)	0.044(1)	0.0364(9)	0.0365(9)	0.029(5)
N	0.95(1)	1.0	0.97(1)	0.95(1)	0.94(1)	1.0
B [Å ²]	0.82(7)	0.5	0.44(9)	1.1(1)	1.0(1)	0.5
O ₁						
x	0.25	0.25	0.25	0.25	0.25	0.25
y	0.6163(5)	0.61(1)	0.622(3)	0.6213(7)	0.6211(7)	0.61(1)
z	0.3906(8)	0.40(1)	0.404(5)	0.383(1)	0.383(1)	0.39(2)
N	0.93(1)	1.0	1.0	0.93(2)	0.93(2)	1.0
B [Å ²]	0.9(1)	1.9	1.9(7)	0.8(1)	0.9(1)	1.9
O ₂						
x	0.4349(1)	0.434(2)	0.4346(7)	0.4299(1)	0.4300(1)	0.431(3)
y	0.7520(6)	0.75	0.749(6)	0.7514(9)	0.7505(9)	0.75
z	0.246(1)	0.25	0.260(6)	0.245(1)	0.247(2)	0.25
N	1.0	1.0	1.0	1.0	1.0	1.0
B [Å ²]	1.14(5)	1.3	1.3(4)	1.22(6)	1.24(7)	1.3
O ₃						
x	0.4376(1)	0.439(2)	0.4372(5)	0.4329(1)	0.4329(1)	0.432(3)
y	0.2461(6)	0.25	0.251(5)	0.2491(9)	0.2490(9)	0.25
z	0.753(1)	0.75	0.766(5)	0.752(1)	0.752(1)	0.75
N	1.0	1.0	1.0	1.0	1.0	1.0
B [Å ²]	1.00(4)	0.6	0.6(4)	1.07(6)	0.93(6)	0.6
O ₄						
x	0.3240(1)	0.327(2)	0.3233(6)	0.3229(1)	0.3229(1)	0.329(2)
y	0.4579(3)	0.460(6)	0.456(2)	0.4551(4)	0.4555(4)	0.454(8)
z	0.9762(8)	0.97(1)	0.998(6)	0.974(1)	0.974(1)	0.96(1)
N	1.00(1)	1.0	1.0	1.00(1)	0.99(1)	1.0
B [Å ²]	1.24(6)	1.3	1.3(4)	1.66(7)	1.67(8)	1.3
	R _P 3.95	R _P 3.79	R _F 8.92	R _P 4.34	R _P 4.43	R _P 2.58
	R _{WP} 5.21	R _{WP} 4.94	R _{WF} 5.28	R _{WP} 5.71	R _{WP} 5.61	R _{WP} 3.31
	R _{EXP} 2.60	GOF 7.70	GOF 1.41	R _{EXP} 2.97	R _{EXP} 3.13	GOF 11.33
	R _F 2.29	R _I 11.96		R _F 2.79	R _F 3.14	R _I 11.55

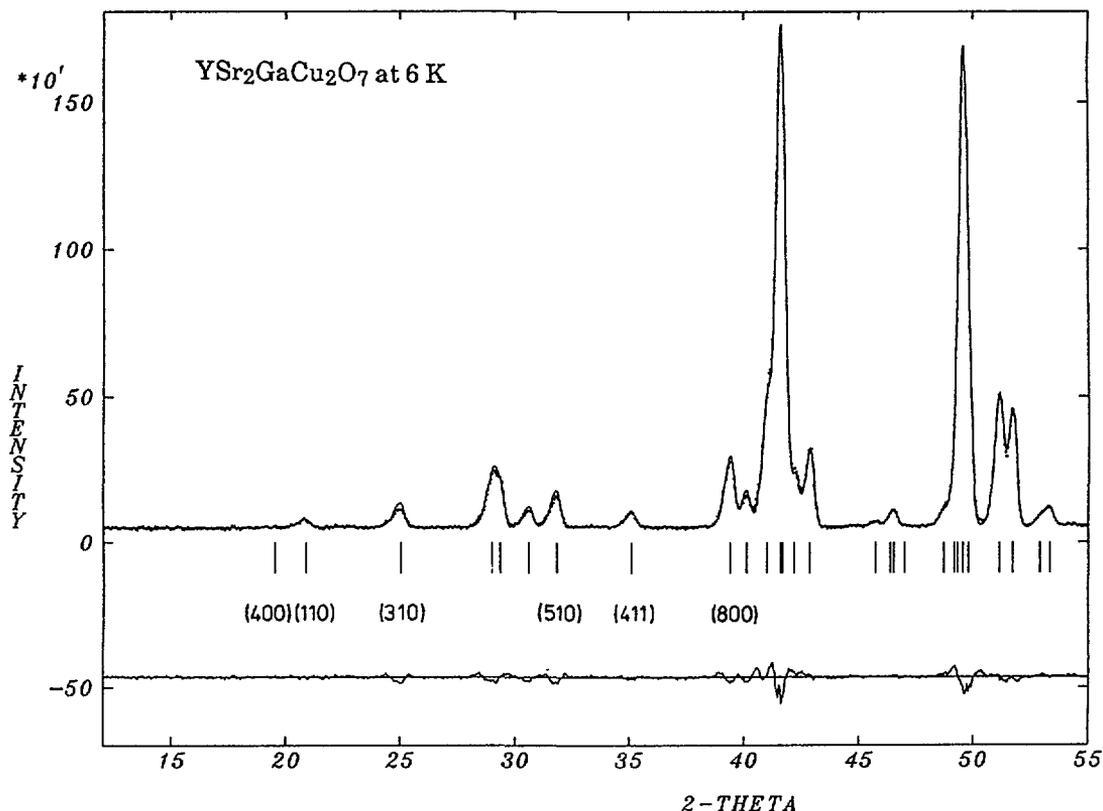


Fig. 3. — Low angle portion of the powder neutron diffraction pattern of $\text{YSr}_2\text{GaCu}_2\text{O}_7$ at 6 K.

refined heavy atom positions clearly suggested a higher symmetry in a larger cell. The final description of the structure was done in space group $\text{Ima}2$ with $a \approx 22.8 \text{ \AA}$, $b \approx 5.5 \text{ \AA}$, $c \approx 5.4 \text{ \AA}$ which was later confirmed by single crystal X-ray diffraction and is also in agreement with powder neutron diffraction results obtained for $\text{YSr}_2\text{GaCu}_2\text{O}_7$ and $\text{NdSr}_2\text{GaCu}_2\text{O}_7$. It is worth noting that space group $\text{Ima}2$ is closely related to $\text{P}4/\text{mmm}$ as well as Pmmm , the space groups of $1\text{-}2\text{-}3\text{-}\text{O}_6$ and $1\text{-}2\text{-}3\text{-}\text{O}_7$ respectively, by simple supergroup-subgroup relations.

To introduce the structure we first discuss the results of the neutron diffraction experiments. The first section of table I gives some experimental details concerning these measurements which were performed on ILL's powder diffractometer D1A. A typical powder neutron diffractogram (here of the Nd-compound at a temperature of 6 K) is shown in figure 2 along with the calculated profile, the difference between observed and calculated profiles and markers for theoretical line positions. The quality of the refinement is quite reasonable as can be seen from the difference curve and also from the reliability factors in table II. Figure 3 shows an enlarged portion of the corresponding diffractogram for the Y-compound at small angles. It is obvious that all observed lines are accounted for by the structural model which is given in table II. The occurrence of reflections like (110), (310), (510) and (710) demonstrates the necessity to choose the enlarged cell of about $22.8 \text{ \AA} \times 5.5 \text{ \AA} \times 5.4 \text{ \AA}$.

Single crystal X-ray diffraction on a particularly small single crystal of $\text{YSr}_2\text{GaCu}_2\text{O}_7$ (see third part of Tab. I for details) also yielded this cell. No violations of the systematic extinctions corre-

sponding to space group $Ima2$ could be detected. Single crystal X-ray reflections profiles (2θ - as well as ω -scans) just resembled the resolution functions of the instrument with no indications of any line broadening or splitting which could have been indicative of structural inhomogeneities or twinning. A difference Fourier synthesis (observed single crystal structure amplitudes minus calculated structure amplitudes derived from the refined structural parameters in Tab. II) was essentially flat with the largest difference peak about 0.5 \AA away from the centre of the strongest scatterer ($Y^{3+} \cdot 36e^-$) and corresponding to a difference density of less than $1.5 \text{ electrons/\AA}^3$.

4. Description of the structure.

Table II gives a compilation of the refined structural parameters for the Y and Nd compound from both the powder neutron as well as the single crystal and powder X-ray measurements. The agreement between X-ray and neutron diffraction results is quite satisfactory. A sketch of the structure is plotted in figure 4 in a perspective view approximately along the $[011]$ direction. This plot is idealized with respect to the oxygen positions for clarity. The dominating features of this structure are, just as in 1-2-3, the bilayers of cornersharing $Cu-O_5$ pyramids separated by Y or RE ions. However, the connection between one bilayer and the next one along the longest axis (a in this setting) is mediated by $Ga-O_4$ tetrahedra sharing two apical oxygen atoms of the $Cu-O_5$ pyramids and connecting to neighbouring $Ga-O_4$ tetrahedra via the two other oxygens (the former "chain-oxygen" of 1-2-3).

Sr fills the large voids located approximately at the x-level of the apical oxygens as Ba does in 1-2-3. A detailed view of the $Ga-O_4$ tetrahedral chains is given in figure 5 in a projection along a . The chains are basically running along c , the diagonal of the 1-2-3 basal plane, but in a zig-zag like fashion. There are two different orientations of the $Ga-O_4$ tetrahedron which alternate along the chain direction.

5. Cation coordination.

Figure 6 shows the local oxygen coordination of the cations in four separate plots. The numbers are distances (in \AA) and angles for the Y-compound at 6 K. The numerical values for selected nearest neighbour cation-oxygen distances (calculated from the results given in Tab. II) including estimated standard deviations are summarized in table III. Only bond lengths from the powder neutron refinements are given because these are superior to the X-ray results with respect to the accuracy of the oxygen positions. The $Cu-O_5$ pyramid (Fig. 6a) involving oxygens O(2), O(3), O(4) (labelled analogous to the conventions introduced by Beno *et al.* [2] for 1-2-3) is fairly regular with four short Cu-O bonds (1.93 \AA and 1.94 \AA) in the basal plane and a long bond (2.36 \AA) towards the apex. Unlike in 1-2-3, the bond angles O-Cu-O deviate strongly from 90 degrees, by as much as 10 degrees for the O(2)-Cu-O(4) angle.

The $Ga-O_4$ tetrahedron (Fig. 6b) consisting of Ga, O(1) and O(4) is symmetry constrained by the mirror plane $m \perp a$ which runs through Ga and the two O(1) atoms. It is also only slightly distorted with two short bonds to the apical oxygen O(4) (1.83 \AA) and two longer ones (1.90 \AA) to O(1) in the $b - c$ plane. The O-Ga-O angles are close to the ideal tetrahedral angle with the exception of O(4)-Ga-O(4), the angle from Ga to the two closest apical oxygens, which amounts to 134.4 degrees. The oxygen coordination of RE (Fig. 6c) is very similar to the Y coordination in 1-2-3 with 4+4 oxygens (O(2) and O(3)) at a distance of about 2.4 \AA (see Tab. III).

Sr is coordinated by 4 oxygens in the basal plane of the $Cu-O_5$ pyramids (O(2), O(3)), by 4 "apical" oxygens (O(4)) and one "chain" oxygen (O(1)) (Fig. 6d). The second O(1) atom is more

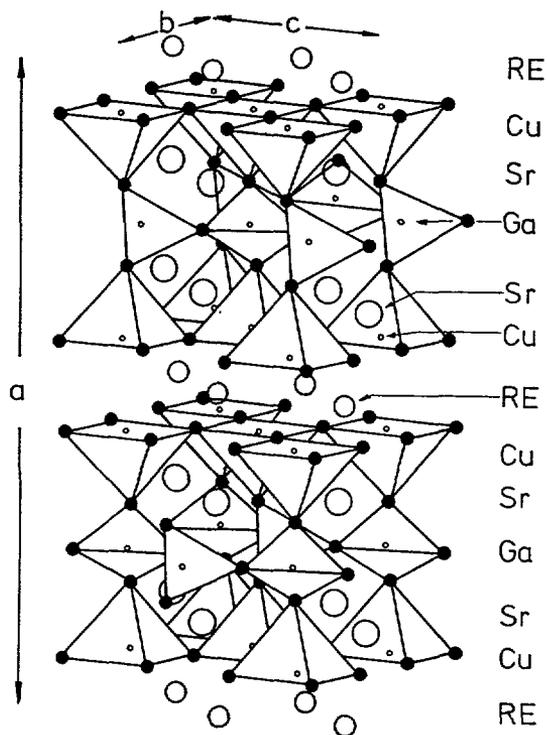


Fig. 4. — Structure of $\text{RESr}_2\text{GaCu}_2\text{O}_7$.

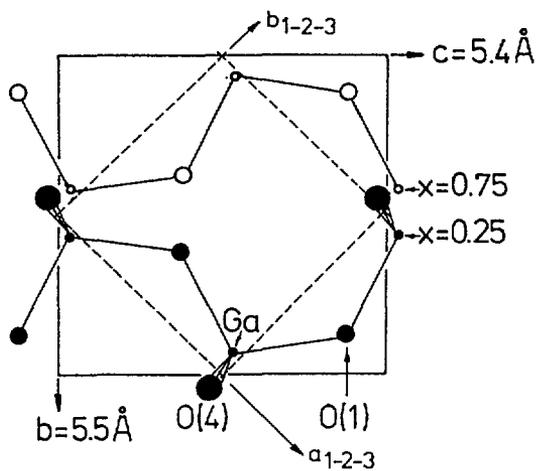


Fig. 5. — Ga-O_4 tetrahedral chain, projected along a .

Table III. — Selected bond distances (Powder neutron data).

	Y, 6 K	Nd, 6 K	Nd, 247 K
Cu-O(2) [Å]	1.933(3) 1.926(2)	1.952(4) 1.940(4)	1.953(4) 1.945(3)
-O(3)	1.937(3) 1.936(3)	1.962(4) 1.942(3)	1.964(4) 1.946(4)
average	1.933	1.949	1.952
-O(4)	2.358(2)	2.317(3)	2.321(3)
Ga-O(1)	1.901(4) 1.898(5)	1.904(5) 1.907(5)	1.907(5) 1.910(5)
-O(4)	2×1.828(4)	2×1.816(5)	2×1.819(5)
average	1.864	1.861	1.864
RE-O(2)	2×2.407(4) 2×2.446(4)	2×2.500(5) 2×2.535(5)	2×2.508(5) 2×2.531(5)
-O(3)	2×2.369(4) 2×2.410(4)	2×2.466(4) 2×2.483(5)	2×2.470(5) 2×2.486(5)
average	2.408	2.496	2.499
Sr-O(1)	2.451(3)	2.468(3)	2.470(4)
-O(2)	2.749(5) 2.791(5)	2.706(5) 2.739(5)	2.721(5) 2.742(5)
-O(3)	2.726(5) 2.753(5)	2.686(5) 2.702(5)	2.691(5) 2.706(5)
-O(4)	2.505(3) 3.102(3) 2.630(5) 2.893(5)	2.521(4) 3.152(4) 2.651(6) 2.925(6)	2.523(5) 3.157(5) 2.651(6) 2.931(6)
average	2.733	2.728	2.732

than 3.5 Å away from Sr and is therefore not considered to belong to the coordination sphere of Sr. Except for these two “chain” oxygens the Sr coordination polyhedron is similar to that of Ba in 1-2-3. However, to our experience the $\text{RESr}_2\text{GaCu}_2\text{O}_7$ structure type does not form with Ba instead of Sr. We believe that the introduction of Sr plays a key role in stabilizing the rather “odd” intergrowth of Cu-O_5 double pyramidal nets with Ga-O_4 tetrahedral chains in this compound because the smaller Sr atom allows the “apical” oxygen O(4) to move towards the alkaline earth site and provide a more regular tetrahedral environment for the Ga atom. The free energy gain associated with this displacement seems to overcome the energy cost due to the severe angular distortion of the Cu-O_5 pyramid, probably because this deformation mode is relatively “soft” as it does not involve any considerable changes of the Cu-O bond lengths.

6. Tilt pattern.

As can be seen in table II the x -coordinates of oxygens O(2) and O(3), forming the approximately square planar base of the Cu-O_5 pyramids are significantly different from each other. Also the apical oxygen O(4) does not lie exactly above or below the Cu atom. These deviations correspond in a first, very rough approximation to a rotation of the Cu-O_5 pyramids around the c -axis. The basal plane is rotated by about 2.6° while the $\text{Cu-O}(4)$ bond direction rotates by as much as 5.6° around c , illustrating the severe distortion of the Cu-O_5 pyramid. This tilt pattern is sketched in figure 7 which only shows the oxygen polyhedra around copper and the Ga position. Arrows indicate the directions of the atomic shifts upon tilting. Complete rows of double pyramids along c rotate in the same direction while the next row in the same plane, being coupled to the first one via the corners of the pyramids, rotate in opposite direction. Also, the sign of rotation alternates in going

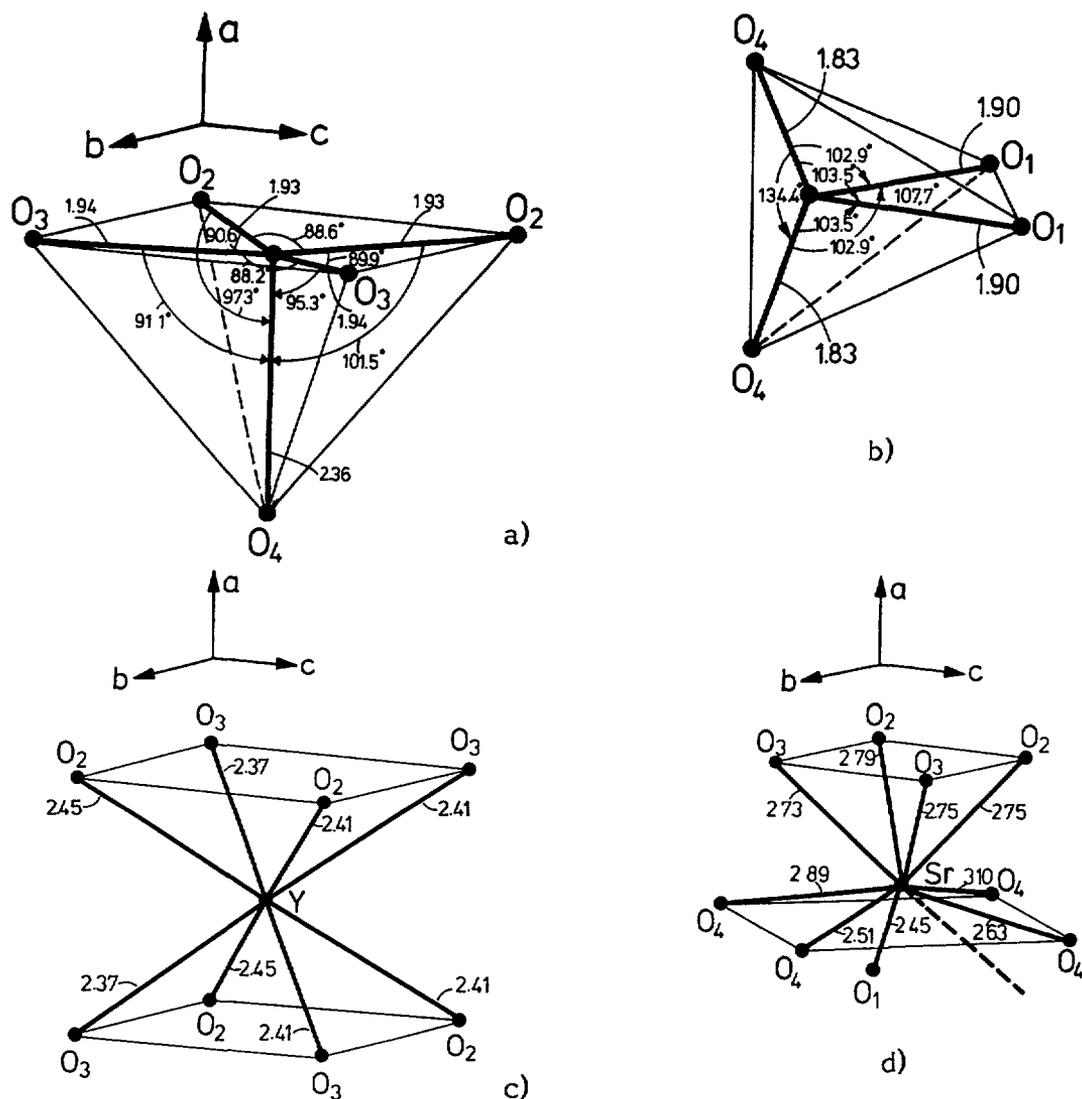


Fig. 6. — Local cation coordination by oxygen for: a) Cu, b) Ga, c) RE, d) Sr. Numbers are distances (in Å) and angles (in degrees).

from one double sheet to the next one along the a axis thus reflecting the doubling of the longest axis compared to 1-2-3. The tilt pattern of the Cu-O-polyhedra in the pyramidal planes closely resembles the corresponding pattern found in the low temperature orthorhombic modification of $(\text{La,Sr})_2\text{CuO}_4$ with the remarkable difference, however, that instead of the distorted Cu-O6 octahedron of $(\text{La,Sr})_2\text{CuO}_4$ a pair of Cu-O₅ pyramids acts as a "rigid body" in $\text{RESr}_2\text{GaCu}_2\text{O}_7$. In $(\text{La,Sr})_2\text{CuO}_4$ a second rotation axis in the same plane but perpendicular to the first one is possible. They both correspond to equivalent directions in the high temperature tetragonal modification and lead to two possible twin orientations in the low temperature form of $(\text{La,Sr})_2\text{CuO}_4$ [22]. In $\text{RESr}_2\text{GaCu}_2\text{O}_7$ the situation is different because the tilting is enforced by the tetrahedral

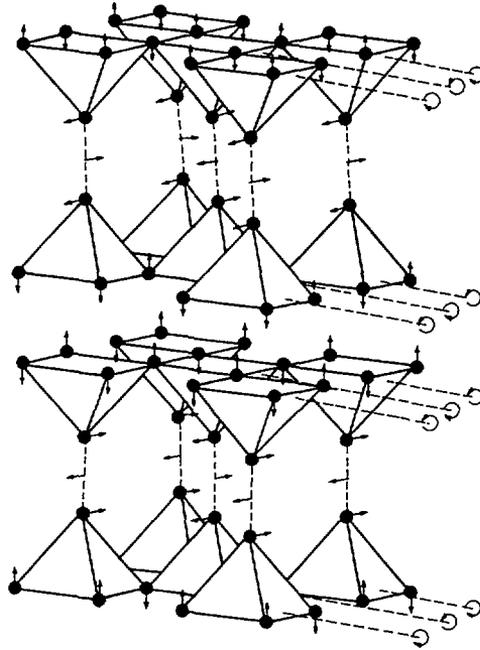


Fig. 7. — Tilt pattern of Cu-O₅ pyramids in RESr₂GaCu₂O₇.

coordination of Ga and the direction of the Ga-O₄ tetrahedral chains determine the tilt direction probably already during crystal growth. The existence of a possible high temperature modification of RESr₂GaCu₂O₇ with zero tilt angle is quite unlikely. At best there might be a disordered form with short segments of chains running either along *b* or *c* and changing direction at point defects. Provided the linear chain segments are sufficiently small (compared to the coherence length of the diffraction experiment), such a pattern would appear to the diffraction experiment as a tetragonal structure with intense disorder within the Ga-O plane and large temperature factors of the atoms belonging to the still locally tilted pyramids. Evidence for such a disordered phase will be given elsewhere [23].

7. Temperature dependence.

The temperature dependence of the structural parameters of RESr₂GaCu₂O₇ was studied for the Nd compound by neutron powder methods (see Tabs. I, II and III). A comparison of the results at 247 K and at 6 K demonstrates that the atom positions are essentially unchanged upon cooling (within one standard deviation) and that there is no structural phase transformation within this temperature range. Only the lattice constants change significantly and, consequently the bond distances change (Tab. III). More interesting, the thermal parameters do not change very much upon cooling. Although they have quite reasonable values at room temperature, they are somewhat larger at 6 K than comparable values for 1-2-3. This might point to small static deformations, either locally or even macroscopically. It should be noted that the structure described in space group *Ima2* is highly symmetry constrained for there are only 8 independent atoms just like in YBa₂Cu₃O₇ but the cell volume is quadrupled. Moreover, the crystal structure is also topologically constrained: The three-dimensional linkage of nets of tetragonal pyramids with tetrahedral

chains leads to severe distortions, particularly of the bond angles, from their ideal values and this could lead to internal strain. However, there is no evidence for a deviation from $\text{Ima}2$ neither from our powder neutron and X-ray work nor from the single crystal X-ray study on an admittedly very small sample. Such deviations, if they should exist at all, would probably first show up as anomalous anisotropic temperature factors of the oxygen atoms, which we hesitate to refine from either of these data sets. Owing to the large unit cell and potential absorption problems in the X-ray case, sufficiently accurate diffraction data would probably require large homogeneous single crystals for single crystal neutron diffraction studies.

8. Structure as a function of rare earth ionic radius.

As already stated in the last paragraph, the structures of $\text{YSr}_2\text{GaCu}_2\text{O}_7$ and $\text{NdSr}_2\text{GaCu}_2\text{O}_7$ are very similar (see structural parameters in Tab. II and bond distances in Tab. III). These two compounds already mark the two extreme cases of a very small trivalent cation and a rather large RE ion and both are close to the stability limits of this structure type with respect to the rare earth ionic radius. Here we briefly discuss some further results of powder X-ray measurements and Rietveld-refinements on $\text{RESr}_2\text{GaCu}_2\text{O}_7$ with various RE ions. The experimental details have already been given in section 2 of table I. A typical powder X-ray pattern (observed, calculated and difference profile) is depicted in figure 8. Table IV gives some structural parameters derived from these measurements. All parameters not shown in table IV may be taken from table II (second column). They are either fixed by symmetry or were deliberately set to these "special" values (like for instance y of $\text{O}(2)$ equal to 0.75) to reduce the number of variables. In each case it had been checked in previous refinement cycles that these values were equal to the "special" ones within one standard deviation. Due to the comparatively small X-ray scattering power of oxygen the estimated standard deviations of the positional parameters of these atoms are quite large and we therefore prefer not to discuss individual cation-anion bond lengths in too much detail. However, we feel that it is worth discussing average cation-oxygen distances derived from these measurements. In figures 9a and b the lattice parameters are plotted as a function of the theoretical RE-O distance calculated from the compilation of ionic radii published by Shannon [24]. The O^{2-} -radius was taken as 1.25 Å. The short axes b and c increase strongly with increasing RE radius, as does the orthorhombicity $2(b - c)/(b + c)$ (not shown). Even more pronounced is the increase of the longest axis a , particularly for the larger RE ions. This general increase of the lattice parameters of course mainly reflects the increasing space requirement of the RE cation. This is demonstrated in figure 10 which shows the observed averaged RE-O distance as a function of the "expected" one. Both quantities correlate nicely and they agree even quantitatively. The Sr-O distance plotted on a similar scale (Fig. 11) on the other hand is almost constant with some small decrease for the larger RE ions. Together with the observation of increased scattering density on the Sr site for the Pr and particularly for the La-compound, this is taken as evidence for a RE-Sr cation disorder for the large rare earths, similar to what has been observed for $\text{La}(\text{Ba}_{1-x}\text{La}_x)_2\text{Cu}_3\text{O}_7$. With increasing RE ionic radius, an increasing amount of RE ions appears to be occupying the Sr site. A corresponding increase of the Sr occupation on the RE site, however, has not been observed. It seems that the compounds with the large RE ions (Pr,La) are slightly off the desired stoichiometry, an assumption which fits to the observation of small amounts of an unidentified second phase in the diffractograms of these compounds. For a detailed investigation of these disorder effects, combined powder X-ray and powder neutron diffraction measurements are in progress [23]. Like the Sr-O distance the average Ga-O distance of 1.86(7) Å (not shown) remains constant within one standard deviation upon doping. In contrast to this the average in-plane Cu-O distance increases significantly with increasing RE radius (Tab.

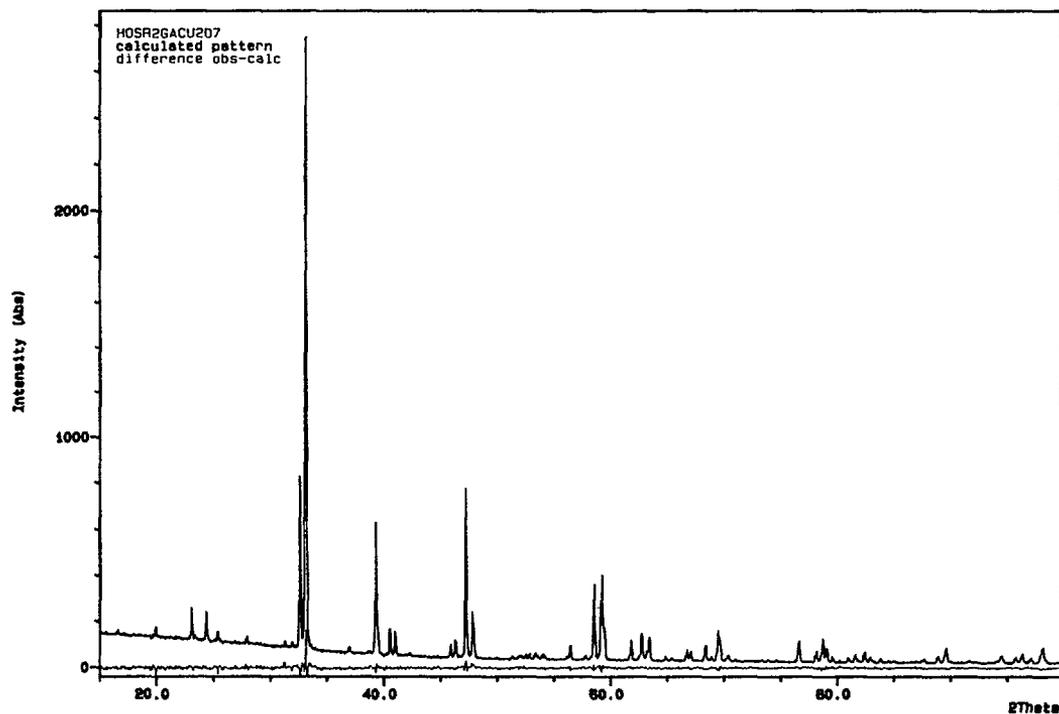


Fig. 8. — Powder X-ray diffraction pattern of $\text{HoSr}_2\text{GaCu}_2\text{O}_7$ at ambient temperature.

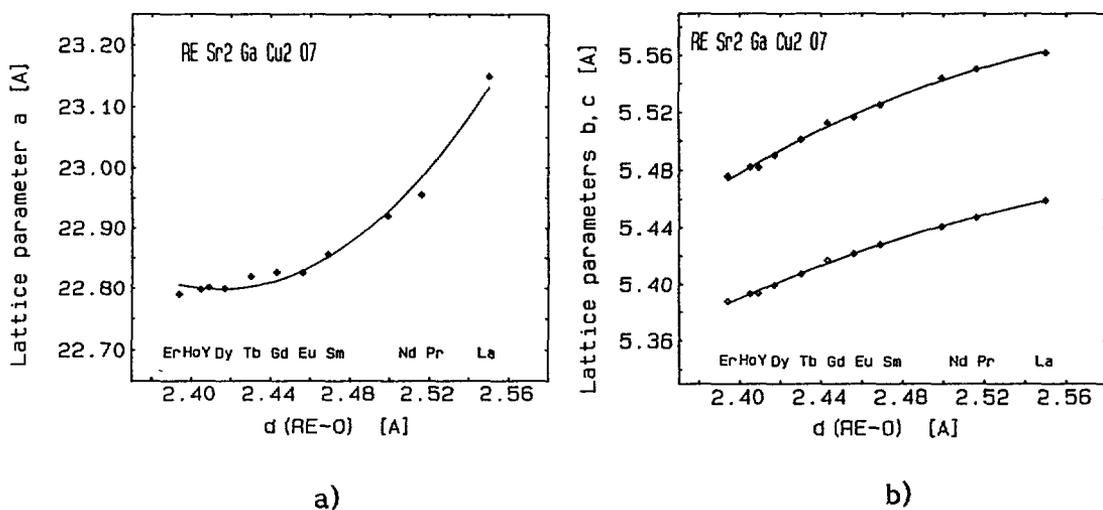


Fig. 9. — Lattice parameters as a function of theoretical average RE-O distance [24] (standard deviations comparable to size of symbols; lines through the points obtained from square regression, intended as a guide to the eye).

Table IV. — Structural parameters as a function of RE-radius (Powder X-ray data).

RE	a [Å]	b [Å]	c [Å]	x Sr	y Sr	x Cu	y Ga	z Ga	y O(1)	z O(1)	x O(2)	x O(3)	x O(4)	y O(4)	z O(4)	R _P	R _I
Y	22.8014(5)	5.4819(1)	5.3936(1)	.3495(2)	.013(1)	.4274(4)	.435(2)	.038(3)	.61(1)	.40(1)	.434(2)	.439(2)	.327(2)	.460(6)	-.03(1)	3.79	11.96
Er	22.7896(7)	5.4762(2)	5.3877(2)	.3499(2)	.012(2)	.4271(6)	.431(2)	.041(3)	.61(1)	.39(2)	.433(3)	.438(3)	.328(2)	.454(7)	-.03(1)	4.34	10.99
Ho	22.7979(7)	5.4822(1)	5.3932(2)	.3494(2)	.010(2)	.4273(5)	.436(2)	.038(4)	.61(1)	.39(1)	.433(2)	.437(2)	.327(2)	.460(7)	-.03(1)	3.69	8.61
Dy	22.7994(7)	5.4902(1)	5.3995(2)	.3493(3)	.012(2)	.4265(6)	.437(3)	.041(4)	.60(1)	.39(2)	.433(3)	.438(3)	.326(2)	.451(7)	-.02(2)	2.20	9.46
Tb	22.8195(5)	5.5009(1)	5.4074(1)	.3495(2)	.009(2)	.4263(5)	.436(2)	.03(1)	.60(1)	.38(1)	.432(2)	.436(2)	.328(2)	.456(7)	-.02(2)	2.62	13.89
Gd	22.8271(1)	5.5126(3)	5.4173(3)	.3490(4)	.011(3)	.4257(8)	.438(4)	.02(2)	.62(2)	.34(3)	.433(4)	.436(4)	.332(3)	.47(1)	-.02(3)	3.04	7.81
Eu	22.826(1)	5.5165(3)	5.4217(3)	.3482(6)	.014(5)	.4271(1)	.441(6)	.03(1)	.58(3)	.41(3)	.432(6)	.438(5)	.329(4)	.47(2)	-.04(2)	2.97	15.28
Sm	22.8559(8)	5.5252(2)	5.4283(2)	.3488(3)	.011(2)	.4254(8)	.433(3)	.032(6)	.62(2)	.38(2)	.429(3)	.436(3)	.327(3)	.448(9)	-.03(2)	2.42	8.26
Nd	22.9201(6)	5.5438(1)	5.4408(1)	.3488(3)	.011(2)	.4246(6)	.438(3)	.029(5)	.61(1)	.39(2)	.431(3)	.432(3)	.329(2)	.454(8)	-.04(1)	2.58	11.55
Pr	22.955(2)	5.5501(3)	5.4473(4)	.3482(5)	.013(4)	.4241(1)	.438(5)	.043(6)	.60(3)	.39(3)	.423(5)	.438(4)	.332(4)	.46(2)	-.04(2)	3.37	16.38
La	23.149(1)	5.5630(2)	5.4577(2)	.3485(3)	.011(3)	.4263(8)	.438(3)	.027(7)	.60(2)	.41(2)	.425(3)	.434(3)	.330(3)	.43(1)	-.06(1)	4.39	12.66

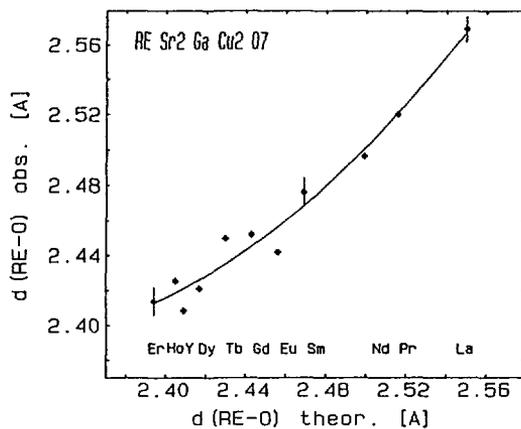


Fig. 10. — Average observed RE-O distance vs. "theoretical" one.

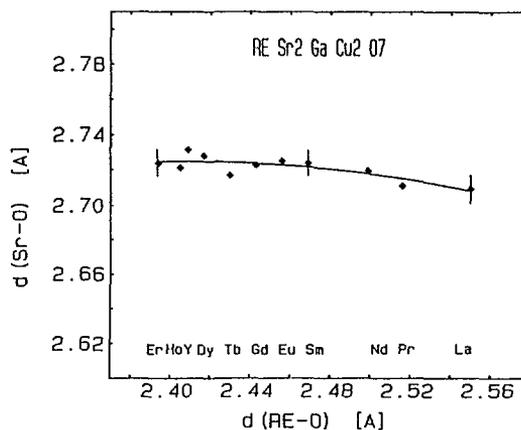


Fig. 11. — Average Sr-O distance vs. theoretical RE-O distance.

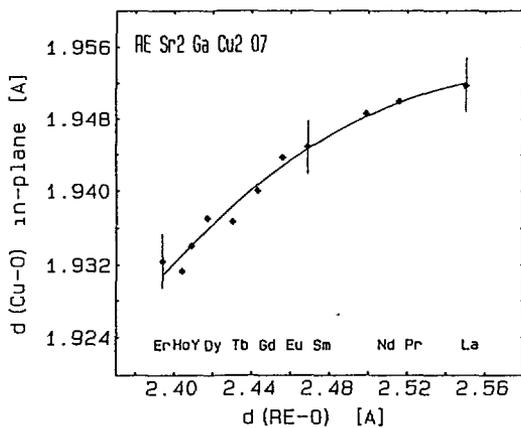


Fig. 12. — Average in-plane Cu-O distance vs. theor. RE-O distance.

III and Fig. 12) and the distance to the apical oxygen correspondingly decreases (Tab. III). The latter statement is mainly based on the powder neutron results for the Y- and Nd-compound. The estimated standard deviations for this distance from the powder X-ray data are much too large to draw such a conclusion but they are at least not in contradiction to it. It is interesting to note that the in-plane Cu-O distances cover, as a function of the rare earth ionic radius, almost the whole range of Cu-O distances observed in the series from semiconducting $\text{YBa}_2\text{Cu}_3\text{O}_6$ to superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$. However, in $\text{RESr}_2\text{GaCu}_2\text{O}_7$, in-plane and apical Cu-O distances are coupled in such a way that the formal oxidation state of Cu (derived from the bond length - bond strength formalism discussed in [25] and using the parameters given therein) is almost constant through the whole series. We find the following approximate values for the "bond valence sums" of the cations:

For RE = Y at 6K :	vCu = 2.17,	vGa = 2.80,	vSr = 1.92,	vY = 2.80
RE = Nd at 6K :	vCu = 2.11;	vGa = 2.83;	vSr = 1.95;	vNd = 2.79
RE = Nd at 247K;	vCu = 2.09,	vGa = 2.81;	vSr = 1.93;	vNd = 2.77

vCu is approximately constant and is always larger than 2.0 while vGa is below 3.0. The effect of temperature is negligible. These bond valence sums could be interpreted in terms of a partial Cu-Ga-disorder (see also next paragraph) amounting to approximately 9 at% Ga on the Cu site and correspondingly about 19% Cu on the Ga site. However, we prefer not to put too much weight on these numbers because the validity of the bond length-bond strength formalism is questionable particularly in cases where Jahn-Teller ions (like Cu^{2+}) or mixed site occupancies (Ga/Cu) are involved.

9. Doping studies.

Various ways of chemical doping have been tried in order to render the compounds, which all are semiconducting when stoichiometric, metallic or even superconducting. "p-type doping" was accomplished by partially replacing Y (or RE) by Ca. Under the preparation conditions given above, the solubility limit checked by powder X-ray diffraction appears to lie somewhere between 15 at% and 20 at% Ca substituted for Y. The specific resistivity drops drastically (from several $\text{M}\Omega\text{cm}$ to about $1.5 \Omega\text{cm}$ for $\text{Y}_{0.85}\text{Ca}_{0.15}\text{Sr}_2\text{GaCu}_2\text{O}_7$ at room temperature). Below room temperature the resistivity upon cooling first increases only gradually but quite rapidly below about 50 K. AC-susceptibility measurements show no traces of superconductivity down to 5 K in any of these samples. A similar behaviour was found for $\text{Gd}_{1-x}\text{Ca}_x\text{Sr}_2\text{GaCu}_2\text{O}_7$. For the Gd and Tb containing compounds we see a pronounced increase of the paramagnetic susceptibility upon cooling below about 20 K, indicating magnetic ordering probably of the RE magnetic moments. Also, the hypothetical solid solution series $\text{Nd}_{1-x}\text{Sr}_{2+x}\text{GaCu}_2\text{O}_7$ was briefly investigated. The solubility appears to be smaller than in the cases mentioned above, a sample with $x = 0.15$ already showed weak lines of a second phase. Partial replacement of Ga^{3+} by Mg^{2+} or Li^+ (nominally $\text{YSr}_2\text{Ga}_{.7}\text{Mg}_{.3}\text{Cu}_2\text{O}_7$ and $\text{GdSr}_2\text{Ga}_{.8}\text{Li}_{.2}\text{Cu}_2\text{O}_7$) and Sr^{2+} by Na^+ or K^+ (nominally $\text{NdSr}_{1.7}\text{Na}_{.3}\text{GaCu}_2\text{O}_7$ and $\text{NdSr}_{1.7}\text{K}_{.3}\text{GaCu}_2\text{O}_7$) did not yield single phase samples. This also applies to our preliminary attempts to "n-dope" these compounds by partially replacing Nd^{3+} by " Ce^{4+} " or Ga^{3+} by Ge^{4+}

The structural characterization of the doped single phase products by diffraction methods will be the subject of a separate paper [23]. Here we only briefly discuss some preliminary results of powder X-ray Rietveld refinements.

As a common characteristic of doped $\text{RESr}_2\text{GaCu}_2\text{O}_7$ samples we find a pronounced positional disorder introduced by doping. This disorder, evidenced by large thermal parameters, mainly involves the Ga-position and its surrounding oxygen atoms. Of course the occupancy of the RE-site (where the substitution is supposed to take place) changes, but quite unexpected, the Sr-site occupation changes as well. In the case of $\text{Y}_{.8}\text{Ca}_{.2}\text{Sr}_2\text{GaCu}_2\text{O}_7$, for instance, the Y- as well as the Sr-site occupancy refines to values less than 1.0 while in the undoped compounds they do not differ significantly from 1.0. As Y and Sr are almost undistinguishable by X-rays (as far as their scattering powers are concerned) this means that the dopant (Ca) which is a weaker scatterer than Y or Sr goes to both the RE and the Sr site. In $(\text{Gd}, \text{Ca})\text{Sr}_2\text{GaCu}_2\text{O}_7$ (where Gd is by far the strongest scatterer) the Sr site occupancy is larger than the equivalent of 1 Sr atom indicating that, upon doping, the RE ion partially goes to the "wrong" site similar to what is observed for the very large RE ions Pr and La already without doping. This unexpected occupational disorder on the Sr site would then quite naturally explain the observed tendency towards positional disorder of the Ga-O₄ tetrahedra because they are adjacent to the Sr site.

Of course, with three different atomic species on each site just one diffraction experiment cannot unambiguously yield the true partial occupancies. We plan to combine powder neutron and X-ray diffraction experiments to clarify this point (which could very well be one of the reasons for the lack of superconductivity in this family of compounds) and also to put the interpretation of individual bond distances on a more quantitative basis.

The most important question concerning structure property relations in these compounds is probably why they are not superconducting or at least metallic. We feel that, at present, we don't nearly have sufficient information at hand concerning both structural as well as physical properties to give a serious answer to this question. We therefore prefer just to name some of the possible reasons one might, on the basis of our present knowledge, think of:

The first (and to our feeling the most probable) reason to name is the possibility of some Ga atoms occupying the Cu-site. It is well established that virtually every dopant which goes to the Cu(2) site in 1-2-3 even in very small concentrations reduces T_c drastically. Unfortunately, the scattering powers of Cu and Ga for X-rays ($27e^-$ for Cu^{2+} , $28e^-$ for Ga^{3+} (at $Q = 0$)) and neutrons (7.72 fermi for the natural mixture of Cu isotopes and 7.39 fermi for Ga [26]) are so close together that we cannot exclude such an occupational disorder of Cu and Ga by diffraction measurements even if it would amount to several at%. A large amount of Ga on the Cu-site and vice versa should, however, manifest itself in additional oxygen positions because the most stable coordination polyhedra are different for the two cations. We have no indication of such additional positions in the undoped compounds, but we again cannot exclude this possibility for the doped ones. Yet another indication for the absence of intense Cu-Ga disorder is the observation (for the undoped specimens) of constant oxygen stoichiometry (see TG results): large amounts of Cu on the Ga site (and the corresponding quantity of Ga on the Cu site) would probably lead to some of the oxygens being weakly bound like in the Cu-O chains of 1-2-3 and therefore to the loss of oxygen at high temperatures. Clearly the important point of possible cation disorder on the Cu and Ga sites needs further clarification by methods other than diffraction.

Another mechanism of occupational disorder, namely the tendency towards occupation of the Sr site by considerable amounts of RE particularly for large RE ions, has already been discussed above. Analogous to $\text{La}(\text{La},\text{Ba})_2\text{Cu}_3\text{O}_7$, this could lead to a reduction of the "effective excess charge" introduced by the doping process.

Furthermore the hole concentration reached so far by doping (estimated by just counting charges) is below the assumed optimum of about 0.15 holes per "active" Cu-site. For $\text{Y}_{.8}\text{Ca}_{.2}\text{Sr}_2$

GaCu_2O_7 for instance, a composition which seems to be at or slightly above the solid solubility limit, the formal Cu-charge would be 2.1, provided the oxygen content stays constant, an assumption which itself is yet to be confirmed by methods other than X-ray diffraction. Simultaneous doping on two different sites might help to further increase the hole concentration but this would make preparation and structural characterization even more complicated.

Apart from these arguments which mainly apply to the doped samples, the undoped structure itself already shows certain peculiarities which could be responsible for the lack of superconductivity: The severe angular distortion of the Cu-O_5 pyramids could point to significant differences in the Cu-O bond character (compared to “ordinary” 1-2-3). Particularly, the apical oxygen O(4) is now bound to Ga by a strong covalent bond which does not point along the longest axis anymore. In 1-2-3 the position of O(4) along c is supposed to reflect the charge transfer from the “chains” to the “planes” and in fact its z -coordinate responds sensitively to changes of the oxygen content [27] and to various kinds of doping [3] and the Cu(2)-O(4) bond distance correlates strongly with T_c [27]. In $\text{RESr}_2\text{GaCu}_2\text{O}_7$ such a variable charge transfer between chains and planes does not occur because the oxidation state of Ga is not variable and the oxygen content is fixed to O_7 .

Also, the difference in symmetry between 1-2-3 and the title compound is to be mentioned in this context: The space group of $\text{RESr}_2\text{GaCu}_2\text{O}_7$, $\text{Ima}2$, has no center of symmetry and the point symmetry of the Cu-site and of its surrounding oxygen sites is 1 whereas in Pmmm (the space group of 1-2-3) Cu(2) and O(2), O(3) and O(4) are on special positions on intersecting mirror planes (point symmetry mm). It is interesting to note that the vast majority of superconductors crystallize in centrosymmetric space groups [28]. On the other hand, there are at least two counter-examples amongst the high- T_c superconductors, namely $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [3], both with space group $\text{Ccc}2$.

The very basic complication with these doping studies is that it is much easier to show a substance to be a superconductor than to prove that it is not possible to make it superconducting. In fact, the number of different ways to dope such a complex compound is huge, as is the number of possible ways to prepare such samples under different conditions and definite statements like “the sample cannot be prepared in single phase form” or “the compound is not superconducting” always relate to the specific preparation conditions used and also largely depend on the obstinacy of the people involved.

10. Comments on possibly related compounds with tetrahedral chains.

First indications of the possible existence of compounds with complete replacement of Cu-O_4 square chains by tetrahedral chains were found in the course of single crystal X-ray studies on a series of partially Sr substituted $\text{YBa}_2\text{Cu}_3\text{O}_7$ grown from BaO- and CuO-rich fluxes in Al_2O_3 crucibles [29]. Refinement of the Ba- and Cu(1)-site occupancies clearly showed a correlation of the Al-content (due to corrosion of the crucible) on the Cu(1)-(chain-) site with the Sr-concentration on the Ba site accompanied by a strong tendency towards disorder of the chain oxygen O(1). The correlation was strongest for the highest Sr-concentrations and pointed at a formulation of a hypothetical solid solution series of the type $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_{1-x}\text{Al}_x\text{Cu}_2\text{O}_{7-\delta}$. The end member $\text{YSr}_2\text{AlCu}_2\text{O}_7$ was then prepared in single phase form by solid state reaction. It crystallizes in a 1-2-3-like apparently tetragonal cell with space group P4/mmm and $a = 3.861(1) \text{ \AA}$, $c = 11.102(3) \text{ \AA}$. Rietveld refinement of X-ray powder data showed pronounced disorder in the basal plane also for this “stoichiometric” compound. It involves both the cation as well as the oxygen site(s) and is so intense that we even can't firmly establish the type of Al-O polyhedra in this substance by X-ray powder diffraction. The same is true for the compound $\text{NdSr}_2\text{FeCu}_2\text{O}_7$ ($a = 3.868(1) \text{ \AA}$, $c = 11.499(3) \text{ \AA}$, space group P4/mmm) which can also be prepared in single phase form. Yet,

both compounds seem to be thermodynamically stable and it is not very likely that they are actually disordered on a scale comparable to the cell dimensions. Most probably these substances consist of a microtwin pattern of ordered domains like for instance in Fe- or Co-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ [5-9] and it is not unreasonable to assume that these domains locally resemble the structure of the title compound $\text{RESr}_2\text{GaCu}_2\text{O}_7$. Just like the transition from orthorhombic to apparently tetragonal symmetry in Fe- or Co-doped 1-2-3, the symmetry gain could be accomplished by stochastic changes of the chain directions, here the Al-O_4 or Fe-O_4 tetrahedral chains, induced for instance by small amounts of residual Cu in these chains. Also, the match between the fairly rigid Cu-O pyramidal nets and the Al-O_4 or Fe-O_4 tetrahedra will probably play an important role. However, all this is still to be confirmed by using local structural probes or by finding out preparation conditions or chemical modifications which allow long range ordering of the chains in the Al- and Fe-compounds.

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