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On the Monoclinic Binary-Layer Compound 'LaCrS₃'

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Abstract

There is a discrepancy between the 'ideal' stoichiometry of the phase LaCrS₃ and the site contents of the unit cell in its structure (La_{7.2}Cr_{6.0}S_{19.2} = 60 La_{1.2}CrS_{3.2}). The authors who determined the

structure [Kato, Kawada & Takahashi (1977). *Acta Cryst.* **B33**, 3437-3443] rationalized this by introducing considerable disorder on the La sites: of the 72 sites, 64 were occupied by La, 4 by Cr and 4 were unoccupied. But this hypothesis has been queried [Makovicky & Hyde (1981). *Struct. Bonding (Berlin)*, **46**, 101-170]. Electron microprobe analyses (EMPA) and density measurements have been made in an

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attempt to resolve the disagreement. While not unequivocal, the results suggest that gross cation disorder is not present and strongly support the notion that the 'LaCrS₃' phase is probably close in composition to La_{1.2}CrS_{3.2} (= La₇₂Cr₆₀S₁₉₂), rather than to LaCrS₃ (La₆₄Cr₆₀S₁₉₂). The former implies an average cation valence of 2.91+ (compared with 3.00+ for LaCrS₃) which, taking into account the method by which the crystals were prepared, is more plausible. [Using similar preparation conditions the binary phases are LaS_{~1.37}(La^{~2.74+}) and ~Cr₅S₆(Cr^{~2.4+}).] The original X-ray data of Kato *et al.* were therefore used to calculate the *R* value and a significantly lower value was obtained for the model with full site occupancy, *viz.* 0.068 compared with 0.091 for the disordered model of Kato *et al.*

1. Introduction

A phase with stoichiometry LaCrS₃ has been reported (Flahaut, 1968, 1979) and studied by powder and single-crystal X-ray diffraction and other techniques (Takahashi, Oka, Yamada & Ametani, 1971; Takahashi, Osaka & Yamada, 1973; Kato, Kawada & Takahashi, 1977; Murugesan, Ramesh, Gopalakrishnan & Rao, 1981). It has been prepared by heating the corresponding oxide, LaCrO₃, in Ar + CS₂ (Takahashi *et al.*) or H₂S (Murugesan *et al.*); the weight change being used to check the (*average*) composition of the product. This, and standard methods of chemical analysis, were said to yield a stoichiometry at least 'close to' LaCrS₃ (Murugesan *et al.*, 1981).

Single crystals were prepared by mineralization of the powder preparations with LaCl₃, CrCl₃ or I₂ (Takahashi *et al.*, 1971, 1973). Single-crystal X-ray diffraction revealed an incommensurate or semi-commensurate layer structure with a large (approximate) unit cell which is triclinic: *a* = 5.94, *b* = 17.2, *c* = 66.2 Å, α = 90.3, β = 95.3, γ = 90.0° (Kato *et al.*, 1977).^{*} In it, two layer types alternate: a two-atom thick (100) layer of *B1* type (LaS), and a three-atom thick (111) layer of *B1* type (or *C6* or *C19* type, CrS₂); *cf.* Fig. 1.

2. The problem and its possible solution

From the number of sites in the unit cell (and due to the mismatch in the *b* direction between the subcells of the two layer types, so that 72 LaS matches 60 CrS₂) the stoichiometry should be La₇₂Cr₆₀S₁₉₂ = 60 La_{1.2}CrS_{3.2}. However, Kato *et al.* (1977) suggested that 4 of the La sites were unoccupied and 4 more were occupied by Cr, so that La₇₂Cr₆₀S₁₉₂ becomes (La₆₄Cr₄□₄)_{Σ72}Cr₆₀S₁₉₂ = La₆₄Cr₆₄S₁₉₂ = 64 LaCrS₃.

^{*} But contrast the parameters of Murugesan *et al.* (1981), which appear to be inconsistent with those of the other workers.

Doubt about the exact stoichiometry of 'LaCrS₃' has been expressed before (Makovicky & Hyde, 1981), when it was suggested that the ideal composition of La_{1.2}CrS_{3.2} was preferable to the LaCrS₃ proposed by other authors. The justification then was that (i) it seemed most unlikely that such an elegantly constructed complex structure would be disturbed and disordered to such a high degree (5.5% of the La sites unoccupied and another 5.5% wrongly occupied by Cr - a total of 11.1%); (ii) this was supported by the considerable difference in bond lengths, La-S = 3.0 and Cr-S = 2.4 Å; (iii) trivalent Cr was unlikely, given the preparation conditions. We reiterate these views, and now consider the matter further.

The reported chemical analyses were on the bulk product from the sulfiding preparations, which may not have been single phase, while the X-ray single-crystal studies were of crystals prepared by vapour-phase transport - and therefore certainly phase-pure, but perhaps only the major (but not the only) phase in the bulk product.

The stoichiometry LaCrS₃ suggests that both cations are formally trivalent, La^{III} and Cr^{III}; and this is said to be supported by various measured properties: the weight change on sulfiding LaCrO₃, and measurements of magnetic, electrical and other

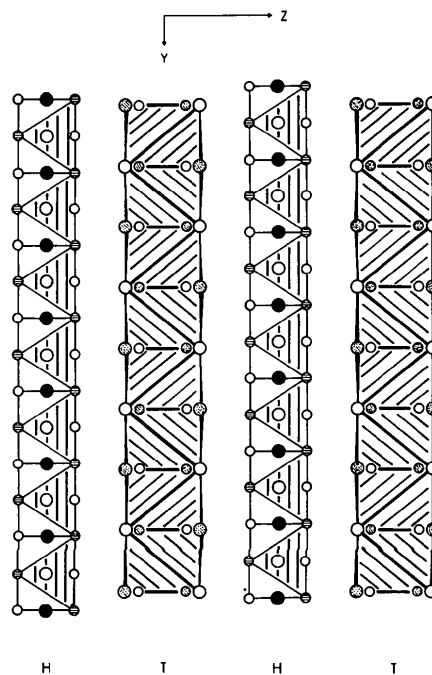


Fig. 1. The layer structure of 'LaCrS₃' idealized to semi-commensurate: parallel to *b*, five units of the (CrS₂) octahedral CrS₂ layers (*H*) match three units of the (SLa₃) square-pyramidal LaS layers (*T*). In the *H* layers the smaller circles are S atoms at *x* = 0 (open) and *x* = ½ (shaded); larger circles are Cr atoms at *x* = ¼ (open) and *x* = ¾ (filled). In the *T* layers the smaller circles are S atoms and the larger circles are La atoms at *x* = ¼ (open) and *x* = ¾ (stippled).

properties (Takahashi *et al.*, 1971, 1973; Murugesan *et al.*, 1981). But we note some room for doubt, *e.g.* the suggestion that 'LaCrS₃' may well be 'non-stoichiometric or impure' (Takahashi *et al.*, 1973). And it seems to us highly unlikely that the preparation conditions (oxide+Ar+H₂S or CS₂ at high temperature) will yield either lanthanum or chromium in their trivalent states but, more plausibly, valences of less than three for both cations. Certainly, our experience in preparing several rare-earth binary and ternary sulfides, and the sulfides of Cr as well as La (always by heating oxides or oxide mixtures in Ar+H₂S at 1250 to 2250 K) is that the stoichiometry of the product is invariably S/M < 3/2. The proposed stoichiometry La₇₂Cr₆₀S₁₉₂ (for 'LaCrS₃') implies a formal average valence of 2.91 (for La and Cr), which is more consistent with this experience.

Also relevant is the reported density of 'LaCrS₃' (Takahashi *et al.*, 1971) which is more consistent with the simpler formula LaCrS₃ (or La₆₄Cr₆₄S₁₉₂) than with our suggested La₇₂Cr₆₀S₁₉₂ (with no defects in the crystal structure); *viz.* $D_m = 4.45 \text{ g cm}^{-3}$, to be compared with $D_x = 4.53$ and 4.75 g cm^{-3} respectively. However, the experimental measurements (Takahashi *et al.*, 1973) also appear to have been carried out on the bulk product from the sulfiding preparation which, as we have suggested, may not be monophasic. [Note that $72 \text{ LaCrO}_3 \rightarrow \text{La}_{72}\text{Cr}_{60}\text{S}_{192} + 12\text{CrS}_x$. The densest chromium sulfide appears to be Cr₇S₈ with $D_x = 4.30 \text{ g cm}^{-3}$, *i.e.* less than that of the ternary sulfide. The densities of the other chromium sulfides, with stoichiometries from CrS to Cr₂S₃, range from 3.89 to 4.21 g cm⁻³. All densities are from the X-ray data of Jellinek (1957).]

The aim of our experimental work (reported below) was to investigate the stoichiometry of well-characterized 'LaCrS₃' specimens as simply and as directly as possible – especially by attempting analysis and density measurements.

3. Experimental techniques

3.1. Sample preparation

The ternary sulfide 'LaCrS₃' has been prepared in several ways: for the present study by the following method. First the pure binary sulfides were separately prepared by inductively heating a graphite crucible containing the pure oxide (La₂O₃, Cr₂O₃, Koch Light, 99.999%) in an atmosphere of flowing argon (95%) + H₂S (5%): temperature ~1650 K. The resulting sulfides were mixed in an approximate molar ratio of 3:2 = LaS_x:CrS_x,* sealed in an evacuated silica-glass tube (20 cm long × 1 cm internal diameter) coated internally with carbon, and then heated for

9 d at 1270 K. From the product single crystals were prepared by vapour-phase transport (using iodine, 3 mg cm⁻³) in a horizontal temperature gradient 1370 → 1220 K for 25 d. The resulting crystals were thin platelets ~1 cm² or so in area, and clearly monophasic.

3.2. X-ray powder diffraction

Diffraction patterns were obtained by means of a Hägg-Guinier focusing camera using strictly monochromatic Cu K α_1 radiation ($\gamma = 1.5405981 \text{ \AA}$) and Si as an internal standard.

3.3. Electron diffraction

Preparations were examined in JEOL 100 CX and 200 CX instruments. The former was fitted with a side-entry goniometer stage ($\pm 60^\circ$) and the latter with an ultra-high-resolution, top-entry stage ($\pm 15^\circ$).

Specimens could not be prepared in the usual way, by crushing, because gross shear and deformation resulted. Clearly, inter-layer cohesive forces (in this extremely lamellar compound) were too weak to prevent slip and/or rotation. The least damaging (though still effective) technique for thinning to electron transparency was powerful ultrasonic dispersion in water. Thin, sheet-like fragments thus prepared were deposited on specimen grids coated with holey-carbon films (which were hardly necessary: many fragments were much larger than the grid mesh).

3.4. Electron microprobe analysis

A number of preparations, suitably mounted and polished, were analysed by energy-dispersive X-ray spectrometry on the TPD microprobe and by wavelength-dispersive spectrometry on the Cameca microprobe (both in the Research School of Earth Sciences at this University). S and Cr were determined from the intensities of their K α emissions, while the La α_1 emission was used for La. For the first instrument data-reduction procedures were similar to those described by Ware (1981), but using routines adapted for sulfide analyses (N. G. Ware, personal communication). For the second, standard routines (supplied by the manufacturer) were used. The instruments were calibrated by the following (synthetic) standards: troilite (FeS), monazite (LaPO₄) and chromium oxide (Cr₂O₃).

Unit-cell contents of La₆₄Cr₆₄S₁₉₂ and La₇₂Cr₆₀S₁₉₂ give stoichiometric ratios La/Cr = 1.00 and 1.20, and S/Cr = 3.00 and 3.20 respectively. Calibrated EMPA analyses using energy dispersive X-ray microanalysis (EDX spectrometry) are widely accepted to have an absolute accuracy of $\sim \pm 1\%$. However, there are two factors which lead to a much higher uncertainty, estimated to be $\sim \pm 5\%$, in the La, Cr and S values reported here. These factors are the following.

* Approximate because the exact stoichiometries of the sulfides were not measured: for LaS_x, $x \approx 1.4$ (*cf.* below), *i.e.* between La₃S₄ and La₂S₃; for CrS_x, $x \approx 1.2$, *i.e.* $\sim \text{Cr}_3\text{S}_6$.

(i) The compounds used for calibration were chemically quite different from the 'LaCrS₃' compound which we investigated. Consequently, data-reduction procedures involved large matrix corrections (of a semi-empirical nature) for every analysis. While large corrections would have minor effects on relative values of chemical composition, absolute values could be somewhat in error.

(ii) Less importantly, due to the relatively poor resolution of energy-dispersive X-ray spectrometry (on the TPD microprobe) the La $L\beta_2$ X-ray peak strongly overlaps the Cr $K\alpha$ peak. This interference is allowed for during data reduction, but with some potential loss of accuracy in the Cr analysis.

(iii) While the wavelength-dispersive mode of the Cameca microprobe resolves the two peaks (La $L\beta$ and Cr $K\alpha$) so that there is no overlap correction, it has a lower take-off angle for X-rays (than the TPD instrument), which results in a larger matrix correction. The net result is a slightly lower accuracy for the Cameca.

We therefore conclude that the uncertainty is ~5%, which will preclude distinguishing the two proposed S/Cr ratios of 3.0 and 3.2, but should still allow a distinction between the two La/Cr ratios of 1.0 and 1.2.

3.5. Density measurement

Despite their large area, the volumes of the single crystals of the 'LaCrS₃' phase, prepared by vapour-phase transport (§ 3.1), were too small (10^{-3} to 10^{-2} cm³) for accurate determination of their density by the Archimedes method. Thicknesses were <20 μ m, and surface steps precluded accurate thickness measurement. They were therefore tested for approximate neutral buoyancy in Clerici solutions (thallium malonate and formate dissolved in water). To attain a sufficiently high density (*i.e.* concentration) it was necessary to dissolve the solutes at 330 K or more. The density of the solution was varied by varying its concentration, and then determined by weighing a known volume (in a calibrated density bottle).

These experiments were not as precise as one would wish: the Clerici solutions are very viscous and, at $T \geq 330$ K, difficult to manipulate to get an accurate density.

4. Results and interpretation

4.1. X-ray powder diffraction

Analysis of the Guinier films yielded the subcell data given in Table 1. Of the 45 observed lines 7 could not be indexed, all being weak or very, very weak.

In Table 1, the lower lines (of bracketed data) are from the literature (Makovicky & Hyde, 1981; based on the results of Kato *et al.*, 1977) while the upper

Table 1. Subcell crystal data

$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	a/b
T cell						
5.934 (2)	5.765 (2)	11.047 (4)	90.15 (3)	95.37 (3)	90.09 (5)	1.029
[5.936]	[5.752]	[11.036]	[90.39]	[95.30]	[90.02]	[1.032]
O cell						
5.936 (2)	3.4311 (2)	11.067 (6)	93.44 (8)	95.27 (5)	90.02 (9)	1.730
[5.936]	[3.435]	[11.053]	[93.29]	[95.29]	[90.03]	[1.728]

lines are our own values. Agreement is good; so that we are undoubtedly dealing with the 'LaCrS₃' phase described and discussed by the earlier workers.

4.2. Electron diffraction

The images obtained were of no help in resolving the problem; so we consider only the diffraction data here.

Because of their extreme morphology a strongly preferred orientation of the crystals on the grid is inevitable: and it will be close to the [001] zone axis. Hence the expected diffraction pattern derives from the reciprocal-lattice mesh of the layers. Such a simple pattern is observed in Fig. 2, which is easily interpreted in terms of the two component meshes: one from the pseudo-tetragonal layers, T , and one from the pseudo-hexagonal layers, H (represented by a pseudo-orthohexagonal reciprocal-lattice mesh, O).

The two (real-space) meshes are shown superimposed (and schematically) in Fig. 3(a), together with the resultant coincidence mesh, C , of the true unit cell. The reciprocal-lattice mesh C corresponding to this (real-space) coincidence mesh is shown in Fig. 3(b), in which the component reciprocal-lattice

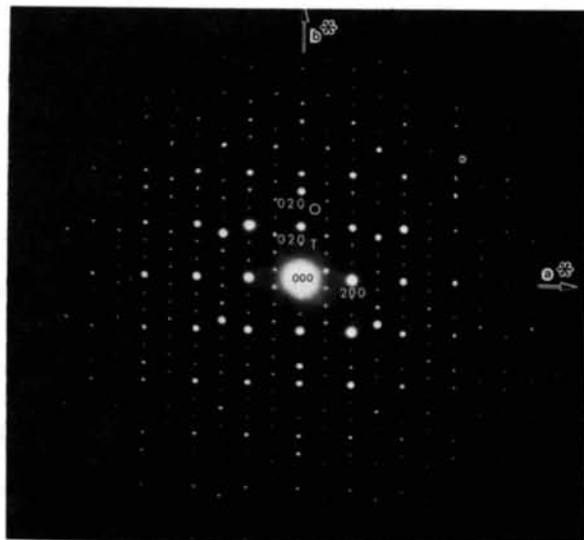


Fig. 2. A [001] zone-axis electron-diffraction pattern of 'LaCrS₃'. The 020 reflections are: T from the pseudo-tetragonal layers, and O from the pseudo-orthohexagonal layers. (The 200 reflection is from both T and H .)

meshes (T and O) are also indicated. Qualitatively, and excluding the expected symmetry-forbidden reflections, this corresponds well with the observed diffraction pattern in Fig. 2.

Quantitatively, the observed pattern (Fig. 2) suggests that $a_T = a_O$ and $b_T = 5b_O/3$, for it appears that the reflections $h00_T$ and $h00_O$ are coincident and that the reciprocal-lattice vectors in the \mathbf{b}^* direction are 'semicomensurate', with $2b_T^*/3 = 2b_O^*/5 = 2b_C^*$. These relations are inconsistent with perfect tetragonal and hexagonal component meshes.

If the T lattice is exactly tetragonal then $a_T = b_T$ and the observed coincidences imply $5b_O/3 = a_O$, so $a_O/b_O = 5/3 = 1.666$. Conversely, if the O lattice is

perfectly hexagonal, $a_O/b_O = \sqrt{3} = 1.732$ and the observed coincidences imply $a_T/b_T = 3\sqrt{3}/5 = 1.039$. The published X-ray data and our own have been given in Table 1: they show $a_O/b_O = 1.730$ [1.728], and $a_T/b_T = 1.029$ [1.032], very close to the ideal values of 1.732, and 1.039 expected for a truly hexagonal H/O lattice. Hence most of the accommodation is provided by distorting the T lattice.†

This is consistent with some other frequently observed diffraction patterns of which an example is shown in Fig. 4. Although superficially far more complex than Fig. 2 it is almost completely accounted for by a threefold repetition of Fig. 2 with 120° (or 60°) angles between the vectors \mathbf{b}^* (and \mathbf{a}^*). (The few remaining reflections can be accounted for by double diffraction.) Such a trilling is more likely for an O mesh with axial ratio very close to the ideal $\sqrt{3}$.

4.3. Electron microprobe analysis

Two sets of analyses, by different instruments, were each internally consistent to a high degree, but the agreement between the sets was much poorer. Expressed as atom ratios relative to Cr the averages were (i) $\text{La/Cr} = 1.200 \pm 0.006$, $\text{S/Cr} = 3.03 \pm 0.01$ (mean of four points from the TPD probe), (ii)

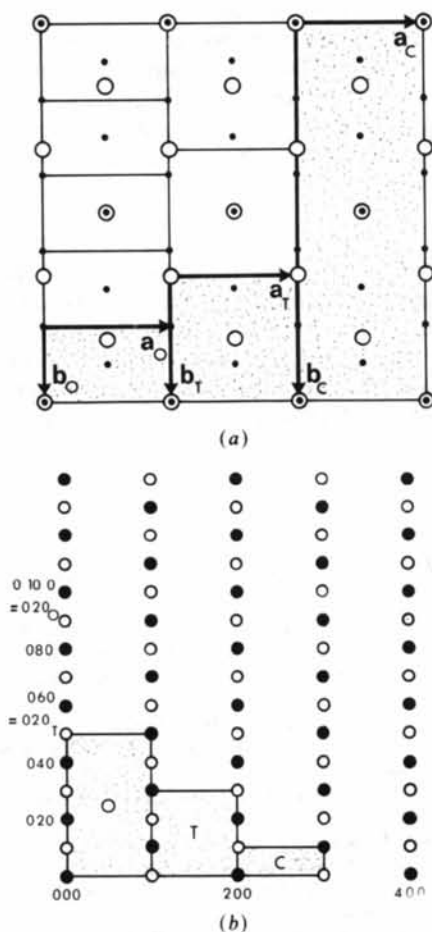


Fig. 3. (a) Projection of the pseudo-orthohexagonal (direct) lattice, O (small, filled circles), and the pseudo-tetragonal lattice, T (larger, open circles), on to the (001) plane of both. Unit meshes are outlined - O on the left, T in the centre, and the composite (coincidence) mesh, C , on the right. One unit mesh of each sort is stippled. (Note that all are centred.) (b) The $[001]$ zone-axis reciprocal-lattice plane corresponding to (a). Due to centring of the real-space meshes, the symmetry conditions are $hk0$, $h+k=2n$ in each case (O , T and C). Hence half the possible reflections are forbidden (open circles). Unit cells are indicated: k indices are for C (no subscript), O and T (subscripts). (The h indices are common to O , T and C .) Compare with Fig. 2.

† Note also that these data give $b_T/b_O = 1.681$ [1.674], which may be compared with the values of 1.680 [1.675] from the X-ray diffraction data. The average from 16 different electron diffraction patterns was 1.69 (3).

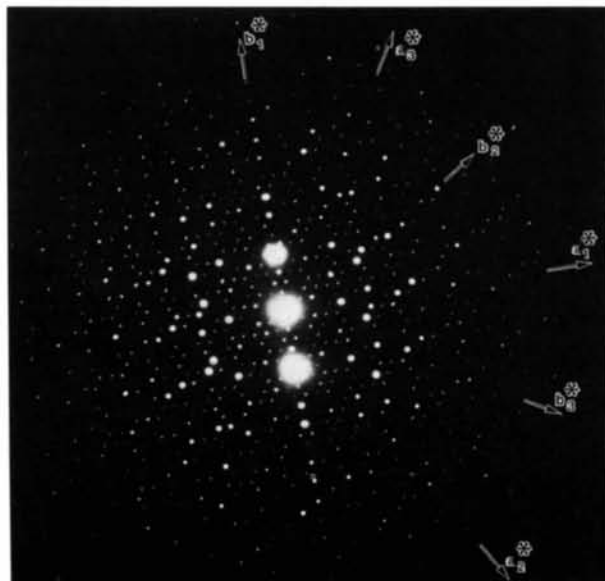


Fig. 4. Another type of frequently observed $[001]$ zone-axis diffraction pattern. It comprises three, equivalent orientations of Fig. 2, differing by 60° ; i.e. $\mathbf{b}_O = \mathbf{b}_H$ parallel to all $\{11\bar{2}0\}_H$. The three equivalent sets of $\mathbf{a}^* + \mathbf{b}^*$ axes are indicated. [The trilling operation involves rotations of $\pm 120^\circ$ (or 60°) about \mathbf{c}^* .]

La/Cr = 1.28 ± 0.01, S/Cr = 3.140 ± 0.002 (mean of three points from the Cameca) and, averaged, La/Cr = 1.23 ± 0.04, S/Cr = 3.08 ± 0.06. [$\Sigma(\text{La} + \text{Cr} + \text{S}) = 98.7$ to 101.9%, indicating that the analyses are acceptable.]

We consider first the ratio La/Cr. The average measured values of 1.20 to 1.28 are, within the expected experimental error of ~5%, equal to the ratio of the numbers of La and Cr sites in the unit cells, *viz.* 1.20; and significantly different from the value of 1.00 proposed by Kato *et al.* This result is strong evidence for the later proposal (La/Cr = 1.20).

The sulfur analyses are lower than expected for La/Cr = 1.20 (*viz.* S/Cr = 3.20), by ~4%, and close to that expected for La/Cr = 1.00 (*viz.* 3.00); but we have reason to suspect that our experimental values are low. Th₃P₄-type γ -'La₂S₃' prepared by the action of H₂S/Ar on La₂O₃ was also analysed by EMPA at the time of the first set of 'LaCrS₃' analyses (i), and using the same standards for La and S. The result was S/La = 1.32 ± 0.01 (average of two points). It is well known that the γ phase has a composition range La₃S₄ to La₂S₃, *i.e.* S/La = 1.33 to 1.50 (Flahaut, 1979), so that in this case the S analysis is clearly somewhat low. If it too were 4% low, the stoichiometry of the prepared lanthanum sulfide would be S/La = 1.37, a more likely figure.

To summarize, EMPA analyses are estimated to have an absolute accuracy of ~±5%. Between the two proposed stoichiometries the ratios La/Cr differ by ~20%, but S/Cr by only ~7%. Hence, both the S/Cr ratio and the La/Cr ratio are consistent with stoichiometry La₇₂Cr₆₀S₁₉₂, but the latter is certainly *not* consistent with La₆₄Cr₆₄S₁₉₂.

We may also note that the average cation valence, deduced from the overall mean of the analyses, is 2.76 ± 0.07, compared with 3.00 for the LaCrS₃ stoichiometry and 2.91 for La_{1.20}CrS_{3.20} (raised to 2.87 ± 0.07 if the S analysis is increased by ~4%, as we suggest it should be).*

4.4. Density

The results are shown in Table 2. They indicate, for the well formed single crystals of 'LaCrS₃', a density in the range 4.61 < D_m < 4.81 g cm⁻³ (*i.e.*

Table 2. *Density measurements*

Density of solution D_m (g cm ⁻³)	Observation†
4.26	s
4.59	s
4.61	s
4.62	n
4.68	n
4.76*	n
4.79*	n
4.81	f

* NB. These two experiments at 338 K; remainder at 333 K.

† f: Crystal floats, s: crystal sinks, n: neutral buoyancy.

$\bar{D}_m = 4.71 \pm 0.08$ g cm⁻³). We recall that it is not certain that the previously reported value $D_m = 4.45$ g cm⁻³ was for a *phase-pure* sample. The values deduced from the X-ray measurements of unit-cell size are $D_x = 4.53$ g cm⁻³ for La₆₄Cr₆₄S₁₉₂ and $D_x = 4.75$ g cm⁻³ for La₇₂Cr₆₀S₁₉₂. Clearly the present data are again consistent with the latter proposal but not with the former.

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* All based on (divalent) S²⁻.