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Preparation and Structure of Fluorite-type $(Sr,Y)Cl_{2.05}$

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Anion excess colorless fluorite-type strontium–yttrium chloride has been prepared. Single crystals of the Sr–Y compound exhibit a primitive cubic lattice with a = 6.967(1) Å. Two mutually exclusive structural models for solutions, neither of which is exact, are discussed. The first is a vacancy model in which the extra charge which results from substitution of Y^{3+} for Sr^{2+} is balanced by the simultaneous removal of a Sr^{2+}–Cl^- ion pair. This model requires individual ion sites to be partially occupied and nonequivalent and is strongly suggestive of vacancy ordering. Refinement in space group $P1$, with sites refined independenty, led to $R = 0.1096$. The second model describes the structure in terms of a Willis cluster of defects and includes both anion vacancies and interstitial anions. Full-matrix least squares refinement in space group $Fm3m$, with positions analogous to those in $UO_{2.12}$ and $(Ca,Y)F_{2.10}$, converged at $R = 0.0633$ for the 114 face-centered parent structure reflections whose $|F|^2 > \sigma(F^2)$. This second model is discussed in relation to a probable true solution which involves longrange order.

Introduction

The fluorite structure is noted for its ability to accommodate high concentrations of chemical defects and to form quality crystals in the presence of heteroion dopants (*1, 2*). $SrCl_2$ has generally been thought to form solid solutions with low concentrations of heteroion dopants, but a recent study of the $SrBr_2$–$SrCl_2$ system indicates that ordered phases, and not solid solution, may prevail (*3*). This structural study was undertaken to reexamine the effect addition of a small amount of trivalent ion has on the $SrCl_2$ fluorite structure.

The effect of addition of $LaCl_3$ on fluorite-type $SrCl_2$ was examined in the late 1950s by Brauer and Müller (*4*). They reported that at 500°C the solubility limit was about 22.5 mole%, that the fluorite structure was retained, and that cell parameters increased by less than 0.03 Å. They postulated that the extra anions were accomodated interstitially at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

In the 1960s, Willis studied by neutron diffraction another mixed valent fluorite phase, UO_{2+x}, where $0 \leq x \leq 0.25$ (*5, 6*). From an analysis of the face-centered reflections of $UO_{2.12}$ he reported that

(a) the cation lattice was unaffected by the presence of excess anions,

(b) excess anions did not occupy the interstitial hole at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$,

(c) anion sites at (x, x, x) were about 90% occupied and were shifted slightly along [111] toward the interstitial holes, and

(d) anions were located interstitially in two other sites located along the [110] and [111] directions, about 1 Å from the center of the hole at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (*5–8*).

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To avoid extremely short anion–anion distances he hypothesized a model which invoked defect clustering. Neutron diffraction studies of other fluorite structures, (Ca,Y)F_{2+x} ($0.10 \leq x \leq 0.32$) seemed consistent with his model (see Fig. 1) (*9–11*).

In a subsequent neutron diffraction study of UO_{2+x}, where $x = 0.25$, the superstructure reflections were examined (*12*). These reflections were found consistent with a bcc cell (space group $I4_132$) whose parameter was 4× that of UO_2. Selected anion displacement along [110] and [111] was confirmed, but the defect clustering hypothesis was not because a small fraction of the cations was found to be shifted from the fluorite sites.

More recently, superstructure reflections evident in powder diffraction patterns of yttrofluorite species in the systems LnF_2–LnF_3 (*Ln* = Sm, Eu, Tm, Yb) and MF_2–REF_3 (*M* = Ca, Sr, Ba; *RE* = Y, La, Sm, Eu, Tm, Yb) have been indexed on the basis of M_mF_{2m+5} and M_mF_{2m+6} homologous series (*13–19*). For the composition region where $m = 13$, 14, 15, or 19, both tetragonal and rhombohedral structures were found and cationic ordering was present. In some of the fluorine-rich rhombohedral phases, anionic ordering is known to exist and in these species anionic clustering occurs as a result of cationic ordering. At intermediate fluorine concentrations, anion clusters appear to be built up from both interstititial and shifted fluorite-structure anions. At fluorine concentrations where cubic symmetry prevails, the microdomains were too small to be revealed by X-ray diffraction, but partial ordering was hypothesized. Later electron diffraction studies of $Ba_4RE_3F_{17}$, an M_mF_{2m+6} species, indicate clearly that the basic symmetry is rhombohedral and that extensive twinning is present at the microdomain level (*19–23*).

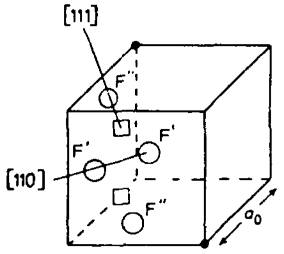

FIG. 1. Clusters in (Ca,Y)F_{2+x}. Above: 2 : 2 : 2 cluster, two *F'* ions, two *F''* ions and two normal ion vacancies (from Ref. (*10*)).

Fluorite-derived structures have also been identified in the CaF_2–REF_3 systems for *RE* = Y, Ho–Lu (*24*). These phases which have an idealized composition of $Ca_8RE_5F_{31}$, i.e., M_mF_{2m+5}, have been indexed improperly on the basis of pseudocubic unit cell parameters approximately 13× that of CaF_2, but properly are rhombohedral with a true geometry $\sqrt{13}$× that of the basic rhombohedral unit cell. More recent phase studies of the systems SrF_2–REF_3, for *RE* = Y, La–Nd, Sm, Gd–Lu indicate either fluorite, fluorite-derived, or tysonite (LaF_3) structures (*25, 26*).

The structure of a fluorite-type crystal of the composition (Sr,Y)$Cl_{2.05}$ prepared in this study is described in terms of both a vacancy and the Willis cluster model. This is the first Willis cluster-type chloride so described.

Experimental

Preparation of (*Sr,Y*)Cl_{2+x}

The method of Taylor and Carter (*27*), dehydration of hydrated chlorides in the presence of excess NH_4Cl, was used to prepare the starting halides. Strontium hydroxide rather than SrO was the reactant for preparation of anhydrous $SrCl_2$. The reaction product, contained in a glass bulb, was cut free from the reaction chamber with a torch and opened in the argon atmosphere of a glove box. Analysis was by X-ray powder diffraction.

To prepare the mixed-valent chlorides, specimens of $SrCl_2/YCl_3$ were mixed in the molar ratio of ~5 : 1, sealed in evacuated, outgassed, quartz ampules, and heated for 2 hr above the $SrCl_2$ melting point (at ~900°C). Crystals grew from the melt as the temperature was lowered automatically to about 400°C at an average rate of 1.5°C/hr. After the products had been annealed at this temperature for several hours or overnight, the furnace was shut off and allowed to cool.

Selected portions of the product, a hard compact mass which adhered to the ampule, were chipped free of the quartz in the glove box and ground lightly in a mortar. The crushed material was transferred to a Schlenk tube fitted with an optical window, and while dried argon flowed through the tube, the sample was examined outside of the glove box under a microscope. Individual crystals were selected and sealed into Lindemann glass capillaries.

To ensure that a single crystal had been selected from the inhomogeneous crushed material, the selected crystals were subjected to microscopic examination under crossed polarizers and only those which did not exhibit birefringence were examined by the precession method. The crystal selected was a colorless, broad, flat wedge whose larger dimensions were ~0.3–0.4 mm.

Data Collection and Refinement

A data set was collected on each of two independently prepared crystals, one set under hexagonal symmetry, the other triclinic. Refinement of the hexagonal data set quickly reached an impasse and was abandoned. The quality of the second crystal was checked carefully. Of the 12 reflections for which half widths were checked, 8 ranged from 0.10 to 0.14°; the remaining 4 had values of 0.16, 0.19, 0.20, and 0.22°. The profile of the 0.19° reflection was slightly asymmetrical. Other crystal data and data collection details for the second crystal are compiled in Table I.

TABLE I

CRYSTAL DATA AND EXPERIMENTAL METHODS FOR $(Sr,Y)Cl_{2.05}$

Crystal system	Cubic, but a triclinic data set was collected
Systematic absences	none
a =	6.967(1) Å
t =	23°C
Formula wt =	160.36
Volume =	338.2 Å^3
ρ calcd =	3.15 g/cm^3

Notes. Thirteen reflections in range $41° < 2\theta < 45°$ for cell refinement. Radiation: Mo$K\alpha$, ($\lambda = 0.70926$ Å); graphite monochromator; scan: θ–2θ; scan width: 1.0° below α_1 to 1.0° above α_2; scan speed: 2.0°/min in 2θ; background count time: 20 sec; $P = 0.02$, $Q = 0$ (see Ref. (*28*)). Reflections measured: h, $\pm k$, $\pm l$; total: 2645; nonzero: 1750; unique primitive: 221; unique face-centered: 114. Standards: intensity of three reflections ($11\bar{1}$, $04\bar{4}$, 044) was measured every 50 reflections. No evidence of crystal degradation was found.

Data were reduced and standard deviations were calculated as a function of counting statistics (*28*). Refinement was undertaken through use of the entire system of Zalkin's programs (MAGPIK, ABSOR, INCOR, ORDER2, FORDAP, LESQ, DISMAT, DISTAN) as modified for local use (*28*), and the program of Busing *et al.* (ORFLS (*29*)).

The maximum symmetry of this data set proved to be primitive cubic. A search for superstructure reflections along the cubic axes was futile, as had been the search along the hexagonal axes in the first crystal ([110] directions in this cubic cell).

Both data collections suffered from severe intensity variations due to absorption. In the second collection a series of azimuthal scans indicated intensity variations of an order of magnitude as ϕ varied over 180°. Seven azimuthal scans were collected at $\chi = 90°$. As χ deviated from 90°, variations as great as fourfold were noted for individual reflections.

Because of uncertainty regarding the accuracy of the absorption correction, first attempts at refinement were made with only a portion of the data, i.e., that collected in the ϕ region where absorption effects were most consistent. To achieve a balance between maximizing the number of data points and minimizing intensity variations, the data were collected into ϕ-dependent "slices" and each slice was averaged in space group *Pm*3 (#200) by ORDER. The data collected over the region $170° < \phi < 205°$ afforded the minimum residual value.

With these data the expected face-centered positions were verified from a Patterson map. Weak peaks were found at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and (0, $\frac{1}{2}$, 0). The only variables, the thermal parameters and the scale factor, refined quickly to a residual $R_1 = 0.2374$ for 97 reflections with $|F|^2 > 2\sigma(F^2)$; $R_1 = \{\Sigma(|F_0 - F_c|)/\Sigma F_0\}$.

A least squares analysis effected with the entire data set merged according to *P*1 symmetry and with all positional and thermal parameters fixed yielded $R_1 = 0.2028$ for 665 data with $|F|^2 > 2\sigma(F^2)$. A difference map revealed only satellite peaks near already positioned atoms. Refinement of only the thermal parameters led to negative values.

All initial refinement attempts had been carried out under the assumption that the additional positive charge of the trivalent heteroion would be balanced by interstitial anions. When these refinement attempts were unsuccessful a vacancy model was hypothesized, even though no definitive evidence for it exists. Charge balance could be achieved by the deletion of ions, i.e., by the removal of three Sr^{2+} ions for every two Y^{3+} ions incorporated, or by paired Schottky defects, with two Sr^{2+} ions and a Cl^- ion removed for every Y^{3+} ion included. Since there are twice as many anion sites as cation sites, if the second mechanism were in operation a 2*x*% reduction in cation occupancy would accompany an *x*% reduction in anion occupancy.

The entire data set was averaged in cubic symmetry, space group *P*23, and atomic positions were input according to the equivalent positions of space group *Pm*3*m*. Thermal parameters, positions, and 100% occupancy were fixed and the scale factor was refined. Next the scale factor, positional, and thermal parameters were fixed and occupancy was refined. A dramatic decrease in the weighted residual after two cycles of refinement suggested partial occupancy of cation sites as a reasonable model for the structure.

To obtain an optimum value for the cation : anion occupancy ratio, several reasonable occupancy values were input in space group *Pm*3*m* and the scale factor was refined for one cycle. A minimum value of the residual was noted for 80% Sr : 90% Cl occupancy and these were chosen as a first approximation of the relative occupancies. Atomic positions were next refined individually, with cycles of refinement alternating between the occupancy, while the thermal parameters and scale factor remained fixed, and the scale factor while the occupancy was fixed. The variations in occupancy and thermal parameters that appeared among the twelve positions suggested that the anions form two interpenetrating tetrahedra of different occupancy. To check further for variable occupancy, refinement in space group *P*1 was effected with the result of only insignificant parameter shifts; $R_1 = 0.0873$ for 117 data with $|F|^2 > 2\sigma(F^2)$.

After the structure analysis had been completed the data crystal and, later, about 30 others which were visually similar to it were analyzed by ICP spectroscopy. For the data crystal, in ppb with the error in parentheses, Sr/Y = 1576(31)/83.1(1.6) = 19.0 ± 0.6. For the 30 visually similar crystals, Sr/Y = 3750(80)/210(4) = 17.9 ± 0.6. The empirical formula is thus assumed to be $MCl_{2.05}$.

The data were also treated in terms of the Willis cluster model (*5–11*) which was developed specifically for anion excess fluorite structures in this composition range. To apply this treatment, the nonface-centered reflections (which were of low intensity) had to be deleted. Refinement under this model proceeded very smoothly. Initial coordinates and occupancy values were input exactly as given for $(Ca,Y)F_{2.10}$: lattice F at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, F' at $(\frac{1}{2}, v, v)$ and F'' at (w, w, w), with $v = 0.36$ and $w = 0.42$ (*10*). Occupancies were set at 1.88, 0.14, and 0.08, respectively.

Refinement was effected in alternating cycles with ORFLS. First, positional, thermal, and anion occupancy parameters were fixed while the scale factor was refined. Then thermal parameters, anion occupancy constrained only to equal 8.20 (4×2.05), the scale factor, and the positional parameters of the displaced anions were refined.

Although fewer parameters were varied in this refinement than in that of the $P1$ vacancy model, this residual quickly fell below that obtained with the vacancy model. After refinement of the site occupancies with ORFLS had stabilized, refinement was continued with LESQ for evaluation of an empirically determined extinction factor. The discrepancy indices were $R = 0.0633$ for 114 data with $|F^2| > \sigma(F)$ and $R_w = 0.0696$. Final cycle refinement parameters are presented in Table II. A final difference map yielded a maximum positive electron density of 1.07 e Å^{-3}. Attempts to refine the entire primitive data set in space group $P\bar{4}3$ as was done for U_4O_9 were unsuccessful (*6*). Observed structure factor tables of both the vacancy and the Willis cluster model are deposited with the NAPS depository.[1]

TABLE II

RESULTS OF WILLIS CLUSTER MODEL REFINEMENT

Atom	Unit cell coordinates	Temperature factor B (Å^2)	Contribution to formula unit
Cl1	0.25, 0.25, 0.25	0.91 (3)	1.74[a]
Cl2	0.5, u, u	6.9 (2.5)	0.24 (3)
Cl3	v, v, v	2.9 (5.1)	0.08 (3)
Sr	0, 0, 0	0.96 (2)	1.0

Notes. $u = 0.402(2)$; $v = 0.341(5)$; extinction factor $= 5.25 \times 10^{-8}$; max shift to error = 0.49.

[a] Reset from 2.05 less concentration of anions in interstitial positions.

To effect a quantitative comparison of the vacancy and the Willis cluster refinements by Hamilton's method (*30*), it was necessary to base both refinements on the same number of data. The vacancy model was therefore refined in space group $F23$; $R = 0.0914$ and $R_w = 0.0711$ for 114 data with $|F| > \sigma(F)$. These values were compared to those for the $Fm3m$ refinement of the Willis cluster model.

It is noteworthy that the data indicate a 3 : 1 : 3 cluster (3Cl1 vacancies and 1 Cl3 [110] and 3 Cl2 [111] interstitials) rather than a 2 : 2 : 2 cluster. This cluster would become by symmetry 3 : 2 : 3. However, the Cl1 and Cl2 occupancies are inversely related and the high temperature factor on Cl2, which may be but an artifact of absorption, precludes rejection of the 2 : 2 : 2 model.

Results and Discussion

When only the face-centered data are considered, Hamilton's test (*30*) substantiates the intuitive conclusion that the Willis cluster model is more accurate than the vacancy model in describing the structure. But the inability of the cluster model to re-

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[1] See NAPS document No. 04061 for 4 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

fine when all the data are considered indicates that although it is a good approximation of the true structure, it is not the definitive solution.

The Willis cluster represents a disordered model. The individual crystals of $UO_{2.12}$ and (Ca,Y)$F_{2.10}$ investigated, respectively, by Willis (*5–7*) and Cheetham *et al.* (*9*) resulted from consideration of only those reflections consistent with face centering. While positions of the interstitial anions were determined precisely, evidence of ordering was not found; clustering was deduced primarily from the physical requirements of atomic sizes.

The $U_4O_9(UO_{2.25})$ phase needs special consideration, for its fluorite-type structure has been studied extensively and refined exactly. For this phase, weak mixed-index superstructure reflections were evident. Willis ascribed these reflections to ordering of the interstitial oxygen atoms, but chose to ignore them. He described U_4O_9 in terms of a disordered model with symmetry $P\bar{4}3$, noting that the majority of the reflections are ascribable to face-centered symmetry. Belbeoch and coworkers (*31*) later determined that the true unit cell was four times as large in each dimension as that of UO_2 and that it was assignable to space group $I\bar{4}3d$. Masaki and Doi (*12*) argue definitely that by using this 4× cubic cell all weak reflections can be assigned to space group $I4_132$. Inclusion of these weak reflections in the refinement process led to the conclusion that both selected cations and anions had moved slighty from the face-centered positions.

The true (Sr,Y)$Cl_{2.05}$ structure probably approximates that of U_4O_9 more closely than it does the Willis cluster, with an obvious difference in the anion occupancy factors. A slight shift in selected cation positions could explain both some of the intensity variations which were evident in supposedly equivalent reflections even after an absorption correction had been made and the satellite peaks found adjacent to atoms already positioned in a difference Fourier. Furthermore, from crystal radii data (*32*) it is apparent that (Sr,Y)$Cl_{2.05}$ is structurally almost identical to UO_{2+x}. The O^{2-}(CN VI)/U^{4+}(CN VIII) ratio is 1.40; the Cl^- (CN VI)/Sr^{2+}(CN VIII) ratio is 1.44. (In the fluorite structure the anion coordination number is 4, but only CN(VI) data are listed for the chloride ion. For consistency CN(VI) data have therefore been used for both anions in the calculations.) Substitution of U^{5+} and Y^{3+} into the respective lattices, with appropriate anion changes, would suggest that the (Sr,Y)$Cl_{2.05}$ structure should approximate that of a UO_{2+x} structure where $x > 0.05$.

The crystal of (Sr,Y)$Cl_{2.05}$ chosen for study unambiguously produced reflections which were inconsistent with face-centered symmetry. In addition, when refinement was freed from the multiplicity constraints of high symmetry, the occupancies were seen to be inequivalent. Both of these observations substantiate the assertion that the true symmetry must be lower than $Fm3m$. An examination of the U_4O_9 data (*12*) suggests that if the (Sr,Y)$Cl_{2.05}$ structure is like that of UO_{2+x}, a scan along the cubic axes would reveal a primitive cubic cell, as was found in the present case. Only by completely scanning a segment of reciprocal space might a 4× cell possibly be observed. A Guiner X-ray powder diffraction photograph was not taken of the (Sr,Y)$Cl_{2.05}$ phase, but one taken of a few crystals of a (Sr,Yb)$Cl_{2.06}$ phase indicated the presence of very weak low angle reflections. Although precession photographs were not taken of a [100] zone, superstructure reflections were not observed in any of the zones examined. However, if these reflections resulted from slight positional perturbation of selected metal and chlorine atoms, and insertion of a few extra interstitial chlorine atoms, it is possible that they would be so weak as to not be seen in the precession photographs taken. In the U_4O_9 work, neutron diffraction data for which the scattering factor of oxygen is about 70% of that of uranium were collected. Hence, the weaker reflections should be appreciably more obvious in the uranium oxide system than in the present work, since the scattering factor of chlorine is only about 50% that of strontium. Examination of a halide crystal in the electron microscope might provide evidence regarding the true unit cell. Evidence for a body-centered UO_2 cubic cell 4× that of the basic cell was seen from the [100] zone in the electron diffraction work of Blank and Ronchi (*33*) and in the $Ba_4Ln_3F_{17}$ work of Greis and Kieser (*21*).

The discrepancy index of the vacancy model is also reasonable; with this model it is possible to refine the entire data set with no significant peaks in the difference map. However, the weak mixed-index reflections contribute marginally to the difference Fourier. Most precedents for vacancy structures are of the NaCl, not the CaF_2 type (*34, 35*).

An alternate interpretation of the data, but one which we could not confirm, is that the crystal is composed primarily of the parent structure with small microdomains of higher anion concentration in which the atomic coordinates are slightly shifted. If the microdomain region were sufficiently small the crystal would appear pristine under the optical microscope. The satellite peaks observed in the difference Fourier could be explained in this manner, as could the significant intensity differences found for supposedly equivalent reflections even after an absorption correction had been applied. The width of all but one of the reflections critically examined on the diffractometer evidenced no indication of a poor quality crystal; but if the microdomains were small enough, they might be invisible even to the X-ray beam, and average intensity data would result. Justification for this model might come from a structural solution based upon the nonface-centered reflections (*36*). However, an examination of the raw data indicated that a successful structural solution based upon these weak intensities was unlikely. One of the strongest mixed-index reflections, $05\bar{2}$, had a value of 266 ± 101, whereas the strongest reflection, 111, had a value of 339 659 ± 2000.

It can be argued that long-range ordering of the $(Sr,Y)Cl_{2.05}$ subcells exists. If absences in the vacancy model occurred on a purely random basis, all sites would be equivalent. Averaging the data to alleviate the absorption discrepancies would tend to make the sites more equivalent rather than less; thus the persistence of the inequivalencies argues for their significance. The obvious inequivalence of both the cation and anion sites, especially in the $P1$ refinement, is strongly suggestive of an ordered structure.

Unfortunately the refinements of these data do not reveal the extended period of the crystal, and while all hypotheses are consistent with a structure based on a fluoritelike subcell, the greater level of confidence and the related structures which adopt it suggest the Willis cluster model to be less incorrect than the vacancy model.

The samples analyzed typically contained a much smaller concentration of trivalent ion than was expected from the starting composition. Walker's work with $SrCl_2$ (*37*) suggests a solubility limit of 5–6% lanthanide trichloride in $SrCl_2$.

In the SrF_2–YF_3 system, a maximum occurs at about the composition $(Sr,Y)F_{2.08}$. If one assumes that the phase diagram of the $SrCl_2$–YCl_3 system is similar to that of the SrF_2–YF_3 system (*26*), and assumes further that the maximum in the phase diagram occurs near the composition 2.05, one can explain the observed behavior. As cooling from the melt took place, crystals of the composition at the maximum formed first.

Because the rate of cooling was relatively rapid (~35°C/day) these crystal had insufficient time to equilibrate with the melt, and remained in the product. Since analysis of visually dissimilar portions of the bulk sample did not identify a fraction rich in trivalent ion, we conclude that some of the MCl_3 component combined with the reaction container either physically or chemically and was discarded with the used ampules.

$(Sr,Y)Cl_{2.05}$ is the first fluorite-type chloride phase which is described in terms of a Willis cluster model and for which primitve reflections have been reported.

Acknowledgments

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