

Structural and Physical Properties of $\text{Cr}_{3\pm x}\text{Se}_4$ ($x \leq 0.20$)

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Received January 2, 1979; in revised form August 1, 1979

The structural, electrical, and magnetic properties of $\text{Cr}_{3\pm x}\text{Se}_4$ ($x \leq 0.20$) compounds are examined. The crystal structure of $\text{Cr}_{2.80}\text{Se}_4$, monoclinic, distorted NiAs type, is determined on a single crystal ($R = 2.9\%$). Physical properties are influenced by the effects of nonstoichiometry. It leads to a separate discussion for compounds $\text{Cr}_{3+x}\text{Se}_4$ ($0 \leq x \leq 0.20$), metallic, antiferromagnetic, with a high g -factor value on the Cr^{2+} site, and $\text{Cr}_{3-x}\text{Se}_4$ ($0 < x \leq 0.20$), poorly metallic and metamagnetic. The results are interpreted on the basis of structural considerations.

Introduction

The compound Cr_3Se_4 has a structure closely related to the NiAs type with an order of the vacancies.

The crystal structure of the monoclinic cell was first determined by Chevreton (1), who showed an alternate localization of the metal vacancies of one out of two of the basic planes of the NiAs substructure. Bertaut *et al.* (2) have established the magnetic behavior of this compound: antiferromagnetic ($T_N = 80$ K) but with an anomalous increase of the susceptibility in high fields due to a rotation of the antiferromagnetic orientation in the field direction. They have determined from $1/\chi$ an extrapolated temperature intercept of -6 K.

Several authors have examined its electrical properties:

— Ivanova *et al.* (3) report semiconducting behavior with a very weak activation energy.

— On the other hand, Babot and Chevreton (4) observe metallic conductivity at high temperature with a metal-nonmetal

transition at 78 K and semiconducting character down to 4.2 K.

— The results of Masumoto (5) also indicate metallic conductivity for Cr_3Se_4 .

It is well known that Cr_3Se_4 has a wide homogeneity range, $\text{Cr}_{3\pm x}\text{Se}_4$ ($x \leq 0.20$), and our purpose in this paper is to study the effect of nonstoichiometry upon the electrical and magnetic properties of this compound.

Experimental

The compounds are first synthesized starting from chromium (99.999%, Johnson Matthey) and selenium (99.999%, Hoboken) in weighted proportions, heated to 1050°C in evacuated silica tubes. The resulting product is pulverized, annealed at 900°C for 2 weeks, and then quenched from 750°C . Under these conditions, the homogeneity range of Cr_3Se_4 , determined from Guinier Lenné photographs, runs from $\text{Cr}_{2.80}\text{Se}_4$ to $\text{Cr}_{3.25}\text{Se}_4$, limited down by the $\text{Cr}_{2+x}\text{Se}_3$ phases and up by the occurrence of Cr_{1-x}Se phases. The least-squares refined

monoclinic cell parameters versus composition are reported in Fig. 1. An anomaly is systematically observed for the composition around $\text{Cr}_{3.05}\text{Se}_4$.

Single crystals are prepared by chemical vapor transport using chlorine as the transport agent. All the crystals have a platelet form, the smallest dimension corresponding to the c -axis of the NiAs subcell.

The magnetic measurements are carried out with powdered samples using a Faraday balance between 77 and 600 K and a Foner vsm magnetometer (0–20 kG) in a temperature range from 4.2 up to 300 K.

The electrical properties are determined on single crystals using the Van der Pauw method.

Crystal Structure Determination

Our first purpose was to investigate the vacancy localization in the $\text{Cr}_{3-x}\text{Se}_4$ compounds. For this reason, we have performed a crystal structure determination on a single crystal with composition $\text{Cr}_{2.80}\text{Se}_4$, in the lower part of the homogeneity range in order to get the highest precision possible.

We have used a single crystal with a platelet shape ($220 \times 80 \times 20 \mu\text{m}$), the cell parameters of which are: $a = 13.132(4) \text{ \AA}$, $b = 6.270(1) \text{ \AA}$, $c = 3.598(1) \text{ \AA}$, $\gamma = 117^\circ 34(1)$, $\beta = \alpha = 90.00(1)$, $Z = 2$. These parameters are related to the NiAs sub-

structure cell by the relations (Fig. 2)

$$a_{\text{monoc}} \approx [(a_{\text{hex}} 3^{1/2})^2 + 2c_{\text{hex}}^2]^{1/2},$$

$$b_{\text{monoc}} \approx a_{\text{hex}} 3^{1/2},$$

$$c_{\text{monoc}} \approx a_{\text{hex}}.$$

The systematic extinctions (hkl with $h+l = 2n+1$) indicate one of the three space groups, Bm , $B2$, $B2/m$. All independent reflections until $2\theta = 65$ (567) have been collected on a P_2 , Syntex four-circle diffractometer using $\text{MoK}\alpha$ radiation.

After absorption corrections (transmission factor from 0.08 to 0.48) the whole set of data is kept for refinement, including the 15 zero intensity reflections in the group $B2/m$.

In the last refinements, the atomic coordinates, the occupancy factors, and the anisotropic thermal coefficients are allowed to vary together (Fig. 3). The final reliability factor, $(\sum |F_{\text{obs}} - F_{\text{calc}}| / \sum F_{\text{obs}}) \times 100$, is equal to 2.9% for the 567 independent reflections with parameter values given in Table I (2.8% without the 15 zero intensity reflections).

The refined formula is $\text{Cr}_{2.80(1)}\text{Se}_4$ or $\text{Cr}_{2.40}^{3+}\text{Cr}_{0.40}^{2+}\square_{0.20}\text{Se}_4^{2-}$ using ionic notation, giving an account of the neutrality of the compound.

We have verified that the normally vacant site in $\frac{1}{2}, \frac{1}{2}, 0$ was completely filled at least within the limit of standard deviation.

The nonstoichiometry with respect to Cr_3Se_4 comes from vacancies on the Cr_I site which is only occupied at 80%.

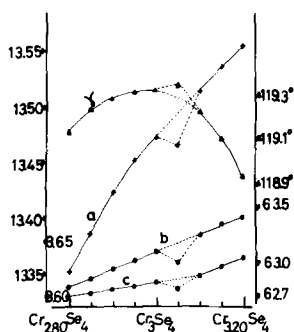


FIG. 1. Cell parameters versus composition in $\text{Cr}_{3\pm x}\text{Se}_4$.

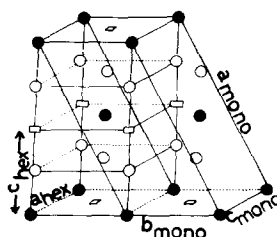


FIG. 2. Relation between hexagonal and monoclinic cell.

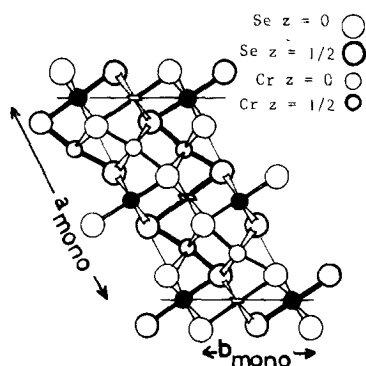


FIG. 3. Crystal structure of $\text{Cr}_{2.80}\text{Se}_4$. Se, $z = 0$, $z = \frac{1}{2}$; Cr, $z = 0$, $z = \frac{1}{2}$. (The solid circles correspond to the Cr partially vacant site.)

The refinements performed using the two other space groups, Bm and $B2$, though they include more variable parameters, do not modify the R values, the atomic positions, or the formula of the compound.

We will compare the structure to the pure NiAs type. In this NiAs substructure with parameters $a = 3.62 \text{ \AA}$, $c = 5.88 \text{ \AA}$ deduced from the monoclinic cell, the Cr atoms would be surrounded by six selenium atoms with six equivalent bonds equal to 2.555 \AA and the Cr–Cr distances would be equal to 2.940 \AA in the c direction (two bonds) and 3.620 \AA in the hexagonal planes (six bonds). Finally there would be two kinds of Se–Se distances, 3.607 and 3.620 \AA .

For the monoclinic superstructure, the distances are reported in Table II. The sites are distorted, especially around the vacant sites. The average values of Cr–Se distances

are, respectively, equal to 2.560 , 2.536 , and 2.518 \AA , around Cr_I , Cr_{II} , and vacant sites with centers at $\frac{1}{2}$, $\frac{1}{2}$, 0 . It should be observed that the Cr–□ distances are considerably shorter than the usual Cr–Cr distances.

In spite of the very low value of the R factor, it is impossible to obtain information concerning any localization of the Cr^{2+} ions and we cannot distinguish between two possibilities: either a statistic disorder between Cr^{2+} and Cr^{3+} (static model) or a mixed valence mechanism (dynamical model).

Magnetic and Electrical Properties

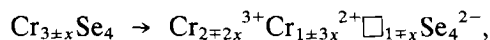
The physical properties lead to separation of the homogeneity range into two parts:

— the first for the compounds with Cr defects $\text{Cr}_{3-x}\text{Se}_4$ ($0 < x \leq 0.20$),

— the second for the compounds $\text{Cr}_{3+x}\text{Se}_4$ ($0 \leq x \leq 0.25$) including the stoichiometric compound Cr_3Se_4 itself.

All the compounds $\text{Cr}_{3\pm x}\text{Se}_4$ exhibit paramagnetic behavior at high temperature ($T > 88 \text{ K}$) following the Curie–Weiss law $\chi = C/T - \theta$.

In Fig. 4, the observed values of the magnetic moment are compared to the theoretical values as deduced from the general formula



which leads to

$$M_{\text{th}}^2 = (2 \mp 2x)\mu_{\text{Cr}^{3+}}^2 + (1 \pm 3x)\mu_{\text{Cr}^{2+}}^2,$$

TABLE I
PARAMETER VALUES^a

	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}
1.6 Cr_I in $2a$	0	0	0	100(12)	98(10)	130(10)	41(8)
4 Cr_{II} in $4c$	0.2566(1)	0.2766(2)	0	118(6)	109(6)	139(6)	49(5)
4 Se_I in $4c$	0.12011(7)	0.4541(1)	0	130(4)	107(4)	138(4)	51(4)
4 Se_{II} in $4c$	0.36702(7)	0.0280(1)	0	125(4)	115(4)	121(4)	63(3)

^a The U_{ij} ($\text{\AA}^2 \times 10^4$) are defined by the formula ($U_{13} = U_{23} = 0$) $\exp(2\pi^2 \sum_{ij} U_{ij} h_i h_j a_i^* a_j^*)$.

TABLE II
 INTERATOMIC DISTANCES

Bond	Multiplicity	Distance (Å)
Cr _I -Se _I	2	2.5436 ± 0.0008
Cr _I -Se _{II}	4	2.5677 ± 0.0006
Cr _{II} -Se _I	2	2.4881 ± 0.0011
	1	2.5075 ± 0.0016
Cr _{II} -Se _{II}	2	2.5821 ± 0.0011
	2	2.5697 ± 0.0016
□-Se _I	4	2.494
□-Se _{II}	2	2.657
Se _I -Se _{II}	2	3.5873 ± 0.0010
	1	3.5700 ± 0.0012
	2	3.6412 ± 0.0011
	2	3.6465 ± 0.0010
Cr _I -Cr _{II}	2	2.9996 ± 0.001
□-□	2	3.595

or replacing μ^2 by their values: $\mu_{Cr^{3+}} = 3.87$, $\mu_{Cr^{2+}} = 4.90$ (supposing quenched orbital moments: $M_{th}^2 = 53.96 \pm 42.08x$).

We see that M^2 values lie above this theoretical curve for the $Cr_{3+x}Se_4$ compounds while they are located below it for the $Cr_{3-x}Se_4$ compounds, a discontinuity occurring for the stoichiometric composition Cr_3Se_4 . Moreover, the extrapolated Curie temperatures θ are systematically negative for the former and positive in the other cases. In the same way, the magnetic order at low temperature and resistivities leads to a separate discussion for each one of the two sets of compounds.

$Cr_{3+x}Se_4$ ($0 \leq x \leq 0.20$)

These compounds are antiferromagnetic as could be expected from the negative values of the θ Curie temperature (Table III). At high temperature, the observed moments, as deduced from the slopes of $1/\chi = f(T)$ curves, give values higher than those calculated from formula I with quenched orbital moments (Fig. 4), but, we note that the theoretical and experimental

TABLE III

θ CURIE AND NÉEL TEMPERATURES FOR $Cr_{3+x}Se_4$ ($0 \leq x \leq 0.20$) COMPOUNDS

	θ_{Curie} (K)	T_N (K)
Cr_3Se_4	-20	88
$Cr_{3.05}Se_4$	-60	82
$Cr_{3.10}Se_4$	-65	51
$Cr_{3.15}Se_4$	-62	26
$Cr_{3.20}Se_4$	-68	21
$Cr_{3.25}Se_4$	-70	15

$M^2 = f(x)$ curves are parallel. It leads to the conclusion that a constant value is added to M^2 from the Cr_3Se_4 composition (equivalent to $Cr_2^{3+}Cr_1^{2+}\square Se_4$ where Cr^{2+} is on 0, 0, 0 positions) or $Cr_2^{3+}Cr_1^{2+}\square Se_4$ in an ionic model.

Supposing that a constant part of the present ions have a higher theoretical moment than the values used in relation I, we can explain this difference (2). We attribute it to this Cr^{2+} ion ($3d^4$) located then in 0, 0, 0 since we know it has a strong tendency to a static Jahn-Teller distortion leading to a Lande factor $g > 2$.

We have drawn in Fig. 4 the curve $M^2 = f(x)$ for the formula $Cr_{3+x}Se_4 \rightarrow Cr_{2-2x}^{3+} \cdot (Cr_{3x}^{2+})_{quenched} (Cr_1^{2+})_{unquenched} \square_{1-x} Se_4^{2-}$, leading to the equation $M_{th}^2 = 42.08x + 59.95$, where $\mu_{Cr^{2+}}$ is calculated by the following formula: $\mu = [4S(S+1) + L(L+1)]^{1/2} = 5.48\mu_B$ for Cr^{2+} (case where multiplet intervals are small compared to kT), which

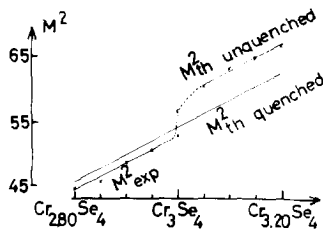


FIG. 4. Theoretical and experimental moments versus composition.

implies a fully unquenched orbital moment corresponding to a Lande factor $g = 2.24$.

A confirmation of this Jahn–Teller effect should be given by a crystallographic analysis in the composition range $\text{Cr}_{3+x}\text{Se}_4$, but, unfortunately, all the crystals we obtained were twinned and unsuitable for crystal structure determination. Nevertheless the good agreement with the calculated moments is strong evidence for such a Jahn–Teller effect. We also observe that the Néel temperature (Table III) decreases as the amount of Cr on the normally unoccupied site increases.

Below the Néel point, we also find for the composition range Cr_3Se_4 – $\text{Cr}_{3.10}\text{Se}_4$ (Fig. 5) the magnetic anomaly observed by Bertaut *et al.* for Cr_3Se_4 . We observe a break in the curves leading to two values of χ ; χ_1 in weak fields and χ_2 in high fields (Fig. 6). The slope change is maximal at $T = T_N$, but still occurs for $T > T_N$. This effect is due to a rotation of the antiferromagnetism direction which tends, under high fields, to become planes perpendicular to this field as indicated by Bertaut, thus increasing the χ values (2). The occurrence of this phenomenon for $T > T_N$ indicates magnetic order above the Néel point which is responsible for the anomaly of the $\chi^{-1} = f(T)$ curves in this region. For the composition up to 3.10 ($T_N < 26$ K) we do

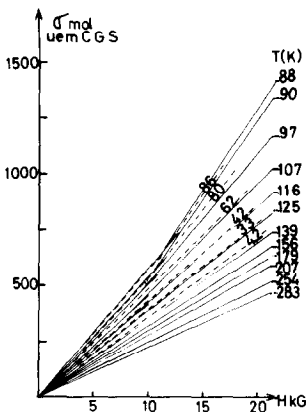


FIG. 5. Magnetization versus magnetic field at various temperatures for Cr_3Se_4 .

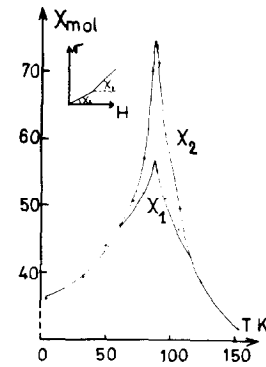


FIG. 6. Susceptibilities χ_1 in low fields and χ_2 in high fields.

not observe this kind of behavior and we find the same slope in weak and high fields (Fig. 7).

The single crystals exhibit poor metallic behavior (Fig. 8) with increases of conductivity associated with the magnetic order transitions and large residual resistivities. Hall measurements indicate n -type carriers.

$\text{Cr}_{3-x}\text{Se}_4$ ($0 < x \leq 0.20$)

At high temperature, the Curie–Weiss law is followed with M values close to the theoretical curve deduced from general formula I. Especially, we do not observe the unquenched orbital moment as in

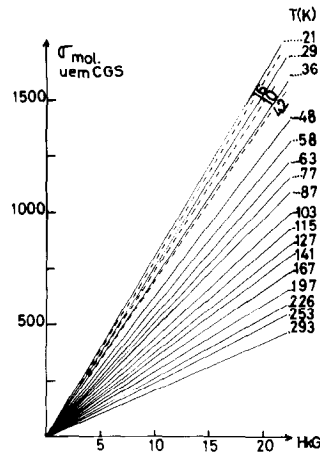


FIG. 7. Magnetization versus magnetic field at various temperatures for $\text{Cr}_{3.20}\text{Se}_4$.

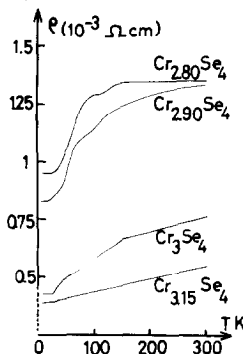


FIG. 8. Resistivities versus temperature for compounds $\text{Cr}_{3+x}\text{Se}_4$.

the $\text{Cr}_{3+x}\text{Se}_4$ compounds. We attribute unquenched moments to pure Cr^{2+} sites and this effect is destroyed by the disorder resulting from the insertion of vacancies. The extrapolated Curie θ values are systematically positive. This means that the vacancy insertion on the 0, 0, 0 site (Cr_I) also destroys the antiferromagnetism coupling on this site.

At low temperature, these compounds exhibit a very high magnetization (Fig. 9). Generally speaking, a moment value of about $2 \mu_B$ is reached at liquid helium temperature in fields of 10 kG. For higher values, there is a weak continuous increase of the moment (Fig. 10). This behavior is characteristic of metamagnetism. The μ values indicate that we are far from complete saturation. In fact, the $n \mu_B = f(x)$ observed values are close to the values calculated

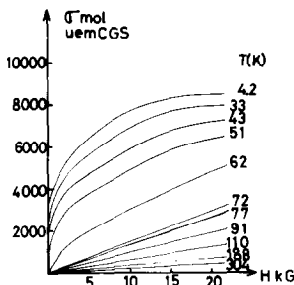


FIG. 9. Magnetization versus magnetic field at various temperatures for $\text{Cr}_{2.80}\text{Se}_4$.

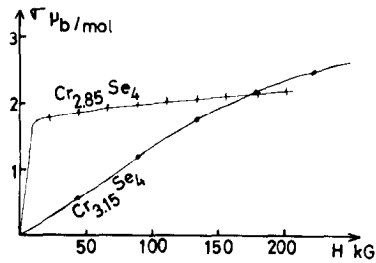


FIG. 10. Magnetization in high fields for $\text{Cr}_{2.85}\text{Se}_4$ and $\text{Cr}_{3.15}\text{Se}_4$.

starting from a model in which the Cr^{2+} ions alone would contribute to the observed moment and the Cr^{3+} contribution would be zero (Table IV).

Two kinds of coupling should be expected, the first with ferromagnetic characteristics between Cr^{2+} ions responsible for the positive extrapolated θ values, and the second antiferromagnetic between Cr^{3+} ions.

The resistivity measurements $\rho = f(T)$ carried out with single crystals are somewhat different from those of $\text{Cr}_{3+x}\text{Se}_4$ phases. The conductivity changes associated with the magnetic ordering are considerably higher. The metallic behavior is much less marked than that for $\text{Cr}_{3+x}\text{Se}_4$, especially for the high x values ($\text{Cr}_{2.80}\text{Se}_4$). The residual resistivity is larger, indicating that additional vacancies on the Cr site in 0 0 0 scatter conduction electrons.

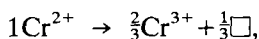
Discussion

For the defective chromium selenide compounds $M_{1-x}X$, the compensation mechanism for nonstoichiometry is

TABLE IV
VALUES $n \mu_B$ VERSUS COMPOSITION

	$n \mu_B \text{ th}$	$n \mu_B \text{ exp}$
$\text{Cr}_{2.90}\text{Se}_4$	2.8	2.65
$\text{Cr}_{2.85}\text{Se}_4$	2.2	2.25
$\text{Cr}_{2.80}\text{Se}_4$	1.6	1.5

provided, starting from $\text{Cr}_1^{2+}\text{Se}_4^{2-}$, by the appearance of Cr^{3+} ions associated with the vacancies following the relation



as is shown by the magnetic measurements. This mechanism is different from that observed in the NiAs chalcogenides of Fe, Co, and Ni in which the nonstoichiometry compensation comes from the formation of $(X-X)^{2-}$ bonds as pointed out by Lupu and Bucur (6). This explains why the homogeneity range is limited to small x values for these latter compounds. The formation of $(X-X)^{2-}$ bonds leads quickly to the pyrite structure.

Contrary to the Cr compounds the limit is reached only for the composition Cr_2Se_3 when all the Cr ions are in Cr^{3+} state, that is to say giving rise to a larger homogeneity range.

The structural description provides a good means for the discussion of the properties of $\text{Cr}_{3+x}\text{Se}_4$. In fact, for $\text{Cr}_3\square\text{Se}_4$, the unoccupied site in $(\frac{1}{2}, \frac{1}{2}, 0)$ must be considered as a normally unoccupied site and not as a vacant site introducing important perturbations in the electronic distribution.

The exchange valency, $\text{Cr}^{2+}-\text{Cr}^{3+}$, introduces a strong differentiation between the cationic sites originally equivalent in the NiAs-type structure. So we will consider separately the two sites: (1) one normally unoccupied in Cr_3Se_4 , and (2) the other on which are localized the second type of vacancies in $\text{Cr}_{3-x}\text{Se}_4$ compounds.

For the first site—on the $\frac{1}{2}, \frac{1}{2}, 0$ positions of the monoclinic cell which is the usual octahedral site of NiAs but deformed—one must suppose a partial occupancy in the $\text{Cr}_{3+x}\text{Se}_4$ compounds. But this occupancy must be considered rather in terms of the presence of an impurity on this site, adding a density of unlocalized electrons leading to a metallic character and a decrease of the Néel point when x increases but not to a qualitative change with respect to Cr_3Se_4 stoichiometry.

This impurity character ceases for $x \approx 0.25$ with the occurrence of a structural change leading to the Cr_{1-x}Se phases.

The second site—on the 0, 0, 0 positions of the monoclinic cell—is partially vacant for the $\text{Cr}_{3-x}\text{Se}_4$ compounds. The introduction of vacancies on this site induces strong perturbations in the physical behavior with respect to Cr_3Se_4 itself.

Moreover, the magnetic structure of Cr_3Se_4 (2) shows that the Cr^{2+} ions are localized on this site and we have pointed out that when the site is completely filled, the magnetic moment measurements (Fig. 4) may be interpreted by an unquenched orbital moment for this Cr^{2+} ion. The presence of vacancies, even in small amounts, induces a sudden quenching of this orbital moment since it occurs very close to the Cr_3Se_4 composition. Our preliminary results of neutron diffraction indicate that it is accompanied by a complete change of the magnetic structure (to be published later), the effect of which is the appearance of metamagnetism.

In $\text{Cr}_{3-x}\text{Se}_4$ compounds, the gradual disappearance of Cr^{2+} ions leads to an attenuation of the metallic character—progressive emptying of the Cr d band—with, at the upper limit for $\text{Cr}_{2.80}\text{Se}_4$, an almost non-metallic behavior with ρ independent of T above the magnetic transition, but again, it is only after a phase transition to the Cr_2Se_3 -type structure that the fully semiconducting character is reached.

In conclusion, in this first paper, we have shown the difference in the Cr_3Se_4 homogeneity range, between $\text{Cr}_{3+x}\text{Se}_4$ on one side and $\text{Cr}_{3-x}\text{Se}_4$ on the other side, and we have proposed an interpretation based on structural considerations.

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