Spinels Renaissance: The past, present, and future of those ubiquitous minerals and materials The systematics of the spinel-type minerals: An overview[†]

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ABSTRACT

Compounds with a spinel-type structure include mineral species with the general formula $AB_2\varphi_4$, where ϕ can be O²⁻, S²⁻, or Se²⁻. Space group symmetry is $Fd\overline{3}m$, even if lower symmetries are reported owing to the off-center displacement of metal ions. In oxide spinels ($\varphi = O^{2-}$), A and B cations can be divalent and trivalent ("2-3 spinels") or, more rarely, tetravalent and divalent ("4-2 spinels"). From a chemical point of view, oxide spinels belong to the chemical classes of oxides, germanates, and silicates. Up to now, 24 mineral species have been approved: ahrensite, brunogeierite, chromite, cochromite, coulsonite, cuprospinel, filipstadite, franklinite, galaxite, hercynite, jacobsite, magnesiochromite, magnesiocoulsonite, magnesioferrite, magnetite, manganochromite, qandilite, ringwoodite, spinel, trevorite, ülvospinel, vuorelainenite, and zincochromite. Sulfospinels ($\phi = S^{2-}$) and selenospinels ($\phi = Se^{2-}$) are isostructural with oxide spinels. Twenty-one different mineral species have been approved so far; of them, three are selenospinels (bornhardtite, trüstedtite, and tyrrellite), whereas 18 are sulfospinels: cadmoindite, carrollite, cuproiridsite, cuprokalininite, cuprorhodsite, daubréelite, ferrorhodsite, fletcherite, florensovite, greigite, indite, kalininite, linnaeite, malanite, polydymite, siegenite, violarite, and xingzhongite. The known mineral species with spinel-type structure are briefly reviewed, indicating for each of them the type locality, the origin of the name, and a few more miscellaneous data. This review aims at giving the state-of-the-art about the currently valid mineral species, considering the outstanding importance that these compounds cover in a wide range of scientific disciplines.

Keywords: Spinel, oxide spinel, sulfospinel, selenospinel

INTRODUCTION

Compounds with spinel-type structure occupy an outstanding position not only in geology, but also in many branches of science, and their crystal structures represent one of the archetype structures based on a cubic close packing of anions. Owing to its quite simple structure type, spinel was one of the very first minerals whose structure has been determined after the discovery of the X-ray diffraction by crystals (Nishikawa 1914; Bragg 1915). Indeed, in the ideal structure topology of spinel, the only variables to be refined are the unit-cell parameter a, a single positional parameter for the anion, the displacement parameters for the three independent sites, and the cation site occupancies. Despite this apparent simplicity, several detailed crystal-chemical studies were carried out on spinels (and on their synthetic analogs), pointing out some interesting crystal-chemical features related to cation disordering with important consequences on their thermo-chemical and physical properties. As an example, the mechanism of incorporation of the cations within the structures, their partitioning as a function of temperature and pressure conditions, the thermal expansion and the compressibility of the spinel structure may be of interest for modeling the Earth's

mantle. In fact, a silicate phase with spinel structure represents the result of the transformation of olivine under high-pressure conditions typical of the transition zone, between 410 and 660 km deep, and this high-pressure polymorph (\gamma-Mg₂SiO₄, also known as the mineral ringwoodite) is considered one of the major phases in the Earth's mantle (e.g., Frost 2008). Besides their enormous petrological importance, spinels are used as geothermometers, geobarometers, and geospeedometers, and they can represent important guides to the mining exploration (e.g., Heimann et al. 2005). Some spinels are ore minerals (e.g., magnetite for iron; violarite for nickel) and others can be used as gemstones. The well-known "balas Ruby" is actually a red-colored variety of spinel, used since long time; some of the most famous gemstones are indeed spinels, e.g., the Black Prince's Ruby and the Timur ruby in the British Crown Jewels. Spinels are actively studied by solid state scientists, for their electric and magnetic properties: it is noteworthy that one of the most common spinels, magnetite, is likely to be related with the discovery of magnetism, as reported by the Roman naturalist Pliny the Elder (23–79 AD). Finally, spinels could form attractive mineral specimens, with octahedral, cube-octahedral, and cubic crystals, sought by mineral collectors and mineralogical museums (Fig. 1).

Mineral phases having a spinel-type structure belong to the chemical groups of oxides and sulfides, and more rarely to selenides, silicates, and germanates. In this paper, we present selected basic data on the 24 known oxide spinels and, for sake of

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[†] Special collection papers can be found on GSW at http://ammin. geoscienceworld.org/site/misc/specialissuelist.xhtml.



FIGURE 1. Specimens of minerals with spinel-type structure. (a) The oxide spinel magnetite, as octahedral crystals with feldspar, from Cerro Huañaquino, Potosi Department, Bolivia. (b) The sulfospinel carrollite, cube-octahedral crystal with calcite from Kambove District, Katanga Copper Crescent, Katanga, Democratic Republic of Congo.

completeness, we report the same data for the 21 known natural sulfospinels and selenospinels, namely sulfides and selenides having a spinel-type structure. For each entry, basic information is given: the type locality, the origin of the name, and a few more miscellaneous data. Moreover, mention is made of recent structural refinements, possibly carried out on natural compounds or, in the lack of it, on its synthetic analog.

CRYSTAL STRUCTURE OF SPINELS

The spinel structure (Fig. 2) is based on a cubic close packing of anions, with cations hosted within tetrahedral (T) and octahedral (M) sites (e.g., Hill et al. 1979). The space group symmetry is $Fd\overline{3}m$, even if some phases show a lowering of symmetry due to the off-center displacement of metal ions along the [111] direction (e.g., Higgins et al. 1975). Cations in tetrahedral and octahedral coordination occupy the 8*a* (point symmetry $\overline{4}3m$) and 16*d* (point symmetry $.\overline{3}m$) positions, respectively. Anions are hosted at the 32*e* positions (point symmetry .3m), which require, for their complete description, an additional parameter, usually indicated as oxygen parameter. The general formula of spinel-type minerals can be written as $AB_2\varphi_4$. For oxide spinels (having $\varphi = O^{2^-}$), the formal charges of A and B cations can be +2 and +3 in the so-called "2-3 spinels" and +4 and +2 in the so-called "4-2 spinels". Considering the sulfo- and selenospinels, having $\varphi = S^{2^-}$ or Se²⁻, there are some uncertainties in the assessment of the actual ion oxidation states, as stressed by Vaughan and Craig (1978). For example, three electronic structure models have been proposed for the synthetic spinel CuCr₂Se₄: Cu²⁺Cr₂³⁺Se₄²⁻ (Goodenough 1967), Cu⁺(Cr³⁺Cr⁴⁺) Se₄²⁻ (Lotgering 1964), and Cu⁺Cr₂³⁺(Se₃²⁻Se⁻) (Lotgering and Van Stapele 1967).

The real spinel-type structures can display variable degrees of disorder of the *A* and *B* cations over the T and M sites. This disorder can be described using the inversion parameter *i*, which is defined as the fraction of the *B* cations at the T sites. The inversion parameter *i* can vary from 0, in the completely normal spinel, ${}^{T}A{}^{M}B_{2}\varphi_{4}$, to 1, in the completely inverse spinels, ${}^{T}B{}^{M}(AB)$ φ_{4} . A totally disordered configuration is obtained for *i* = 0.67.

Oxide spinels

Oxide spinels include 24 different mineral species (Table 1) that can be classified as "2-3 spinels" ($A^{2+}B_2^{++}O_4$) and "4-2 spinels" ($A^{4+}B_2^{2+}O_4$). Considering the "2-3 spinels", the various mineral species can be grouped as a function of the dominant B^{3+} cation, forming four different groups, characterized by Al, Cr, Fe, and V as *B* cation. "4-2 spinels", rarer than the former group, has Fe²⁺, Mg²⁺, and Mn²⁺ as *B* cation, whereas the *A* cation is represented by a tetravalent cation (Si, Ti, and Ge) or by a combination of pentavalent and trivalent cations, like in filipstadite. In the following we describe the oxide spinels sorted alphabetically.

Ahrensite—**SiFe**₂**O**₄. Ahrensite is a silicate spinel, the Fe^{2+} analog of ringwoodite and the most recent entry among minerals with the spinel structure. It has been found in the Tissint Martian meteorite recovered in Morocco in October 2011 (Ma et al.



FIGURE 2. Spinel structure, with the cubic cell outlined. Octahedral and tetrahedral sites are shown in dark gray and light gray, respectively.

2013). The name honors Thomas J. Ahrens, geophysicist at the California Institute of Technology. Crystal structure of synthetic $SiFe_2O_4$ spinel was refined by several authors (e.g., Yagi et al. 1974; Yamanaka et al. 2001).

Brunogeierite-GeFe2O4. Brunogeierite was first described from Tsumeb, Namibia (Ottemann and Nuber 1972). There were some uncertainties about the oxidation state of germanium and iron in this mineral. In the type description, electron-microprobe data were presented with all germanium given as GeO₂; however, after Fleischer and Mandarino (1995), the mineral was assumed to have ideal formula Ge2+Fe2+O4, and this formula was reported in most mineralogical treatises and compilations, even if the +2 oxidation state of germanium is unlikely in natural phases. Cempírek and Groat (2013), on the basis of bond-valence calculations carried out using a structural model of brunogeierite obtained with single-crystal X-ray diffraction data (Welch et al. 2001), redefined the correct chemical formula as $Ge^{4+}Fe_2^{2+}O_4$. Brunogeierite has been named after dr. Bruno H. Geier (1902-1987), formerly chief mineralogist of the Tsumeb Corporation. Brunogeierite is a germanate spinel.

Chromite—**FeCr**₂**O**₄. The name chromite was introduced in the mineralogical literature by Haidinger (1845) in allusion to its composition. The type locality is considered Gassin, Var, France (Gallitzin 1801). Today the term chromite refers to the Fe endmember along the join MgCr₂O₄–FeCr₂O₄; synthetic binary join was studied through single-crystal X-ray diffraction by Lenaz

 TABLE 1. Oxide spinels: Valid mineral species, ideal chemical composition, and selected structural data

	Mineral species	Chemistry	a (Å)	<t-o> (Å)</t-o>	<m-o> (Å)</m-o>	Ref.
		2-3 spinels	$(A^{2+}B_2^{3+}O_4)$	1		
$B = AI^{3+}$	Gahnite	ZnAl₂O₄	8.085	1.953	1.912	(1)
	Galaxite	MnAl ₂ O ₄	8.181	1.991	1.927	(2)
	Hercynite	FeAl ₂ O ₄	8.154	1.968	1.928	(3)
	Spinel	MgAl ₂ O ₄	8.083	1.914	1.931	(4)
$B = Cr^{3+}$	Chromite	FeCr ₂ O ₄	8.376	1.997	1.994	(5)
	Cochromite	CoCr ₂ O ₄	8.335	1.963	1.996	(6)
	Magnesiochromite	MgCr ₂ O ₄	8.333	1.965	1.995	(5)
	Manganochromite	MnCr ₂ O ₄	8.437	2.031	1.998	(7)
	Zincochromite	$ZnCr_2O_4$	8.327	1.967	1.991	(8)
$B = Fe^{3+}$	Cuprospinel	CuFe ₂ O ₄	8.394	1.890	2.057	(9)
	Franklinite	ZnFe ₂ O ₄	8.442	1.978	2.027	(10)
	Jacobsite	MnFe₂O₄	8.496	2.001	2.035	(11)
	Magnesioferrite	MgFe₂O₄	8.384	1.910	2.043	(12)
	Magnetite	FeFe₂O₄	8.397	1.886	2.061	(13)
	Trevorite	NiFe ₂ O ₄	8.347	1.877	2.048	(14)
$B = V^{3+}$	Coulsonite	FeV_2O_4	8.453	1.991	2.025	(15)
	Magnesiocoulsonite	MgV₂O₄	8.42	1.954	2.032	(16)
	Vuorelainenite	MnV_2O_4	8.52	2.041	2.023	(17)
		4-2 spinels	s (A ⁴⁺ B ₂ ²⁺ O ₄))		
$B = Fe^{2+}$	Ahrensite	SiFe ₂ O ₄	8.234	1.652	2.137	(18)
	Brunogeierite	GeFe ₂ O ₄	8.413	1.771	2.132	(19)
	Ulvöspinel	TiFe₂O₄	8.532	2.006	2.046	(20)
$B = Mg^2$	2+ Qandilite	TiMg₂O₄	8.438	1.980	2.025	(21)
	Ringwoodite	SiMg₂O₄	8.071	1.665	2.066	(22)
$B = Mn^2$	2+ Filipstadite	(Sb _{0.5} Fe _{0.5})	8.463 (×3)	2.029ª	2.076 ^a	(23)
		Mn_2O_4				

Notes: (1) Ardit et al. 2012; (2) Essene and Peacor 1983; (3) Lenaz and Skogby 2013; (4) Redfern et al. 1999; (5) Lenaz et al. 2004; (6) Garcia Casado and Rasines 1986; (7) Raccah et al. 1966; (8) O'Neill and Dollase 1994; (9) Mexmain 1971; (10) Pavese et al. 2000; (11) Lucchesi et al. 1997; (12) Andreozzi et al. 2001; (13) Fleet 1984; (14) Blesa et al. 1993; (15) Reuter et al. 1969; (16) Reuter et al. 1983; (17) Plumier 1962; (18) Yagi et al. 1974; (19) Welch et al. 2001; (20) Bosi et al. 2009; (21) Wechsler and Von Dreele 1989; (22) Hazen et al. 1993; (23) Bonazzi et al. 2013. ^a Average bond distances of T and M sites weighted taking into account the different multiplicities of the individual sites (Bonazzi et al. 2013). et al. (2004) and through Raman spectroscopy by Lenaz and Lughi (2013). Due to the extensive solid solution between the two end-members, it is likely that several alleged occurrences of chromite actually consist of magnesiochromite, the Mg endmember. Moreover, chromite forms solid solutions with other oxide spinels, like hercynite, spinel, magnetite, coulsonite, zincochromite, cochromite, and manganochromite. Recent structural refinements of natural chromites from the Bushveld Complex, South Africa, are reported by Lenaz et al. (2007).

Cochromite—CoCr₂O₄. Cochromite was first described from the Bon Accord nickel deposit, Barberton, South Africa (De Waal 1978), in a trevorite-liebenbergerite-bunsenite metamorphic assemblage, as a relict phase rimmed by trevorite. This is the only known occurrence. The name is after its chemical composition. At the type locality, Co^{2+} is partially replaced by Fe^{2+} and Ni²⁺. Some samples have Ni > Co, and potentially represent a distinct mineral species, NiCr2O4. Indeed, De Waal (1978) called that phase "nichromite", but it was never submitted to the IMA CNMNC for approval; therefore "nichromite" is not considered a valid mineral species (and for this reason it is omitted from the present compilation). More recently, another Co-rich spinel was described from Bo Ploi, Thailand (Guo et al. 1994). Its end-member composition is CoAl2O4 and this could represent another distinct species. Crystal structure data on cochromite are not available but Garcia Casado and Rasines (1986) refined the structure of synthetic CoCr₂O₄. Structural data on synthetic CoAl₂O₄ are known as well (Ardit et al. 2012).

Coulsonite—FeV₂O₄. The original description of coulsonite was made on a sample from Bihar, India (Dunn 1937) as patches in magnetite, intergrown with ilmenite and replaced by hematite. The name honors Arthur Lennox Coulson (1898-?), geologist of the Indian Geological Survey. Owing to the poor characterization of this mineral, it was also hypothesized that coulsonite from Bihar could be nothing but vanadium-bearing maghemite (Frankel and Grainger 1941). Then, coulsonite was redefined and properly characterized after a new occurrence at the Buena Vista Hills, Lovelock, Nevada, U.S.A. (Radtke 1962). Crystal structure data on coulsonite are not available, whereas Reuter et al. (1969) refined the crystal structure of synthetic FeV₂O₄.

Cuprospinel—CuFe₂O₄. Cuprospinel was first described by Nickel (1973) from the heavily oxidized dump of the Consolidated Rumbler mines Limited, near Baia Verte, Newfoundland, Canada, in close association with hematite; this is the only known occurrence. Name is after its chemical composition. The investigation showed that the dump was originally formed by Cu-Zn ore that had ignited spontaneously and smouldered at intervals. Consequently, cuprospinel formed under particular environmental conditions. Crystal structure data on cuprospinel are not available but the crystal structure of synthetic $CuFe_2O_4$ was refined by Mexmain (1971).

Filipstadite—(Sb_{0.5}Fe_{0.5})Mn₂O₄. The mineral was first described from Långban, Värmland, Sweden (Dunn et al. 1988) and named after the city of Filipstad, near which the Långban mine is located. The ideal chemical formula is $(Sb_{0.5}^{+}Fe_{0.5}^{++})(Mn^{2+},Mg)_2O_4$. The oxidation state of manganese, antimony, and iron is assumed on crystal-chemical and stoichiometric grounds. Sb⁵⁺ and Fe³⁺ must share the same site and this is a case of valency-imposed double site-occupancy (Hatert and Burke 2008). A recent and

accurate structural study of filipstadite was carried out in a cubic supercell with a cell edge three times longer than the normal one (Bonazzi et al. 2013). The comparison of new electronmicroprobe data and single-crystal X-ray diffraction data led Bonazzi et al. (2013) to propose a quite complex distribution of cations over six M and five T sites in the supercell.

Franklinite—ZnFe₂O₄. The mineral was first described by Berthier (1819) and named after its type locality, the Franklin mine, New Jersey, U.S.A. Both the mine and the mineral took their name in honor of the scientist and statesman Benjamin Franklin (1706–1790), one of the founding fathers of the United States of America. At the type locality, franklinite contains minor Mn²⁺ substituting for Zn²⁺. Crystal structure refinements of ZnFe₂O₄ spinel, both natural or synthetic, have been reported by several authors (e.g., Lucchesi et al. 1997, 1999; Pavese et al. 2000), indicating a normal cation distribution.

Gahnite—ZnAl₂O₄. First described by von Moll (1807) from the Falun copper mine, Dalama, Sweden, gahnite was named after the Swedish chemist and mineralogist Johan Gottlieb Gahn (1745–1818). The crystal structure of gahnite from the type locality was solved by Saalfeld (1964) and several structural refinements are known, both on natural (e.g., D'Ippolito et al. 2013) and synthetic ZnAl₂O₄ [Rietveld method on powder: Popović et al. (2009); single crystal: Ardit et al. (2012)].

Galaxite—MnAl₂O₄. This mineral was first described by Ross and Kerr (1932) from a vein containing unusual Mn minerals equilibrated under amphibolites facies conditions near Bald Knob, North Carolina, U.S.A. It was named galaxite to distinguish it from the synthetic analog, manganspinel, described by Krenner in 1907 from an iron-furnace slag (Spencer 1922, and references therein). The name recalls galax that grows abundantly in North Carolina, and the city of Galax, Virginia, where Mr. Crabill lived. He had long been interested in the geology and mineralogy of the type locality of galaxite, and he had often given his assistance to visiting geologists. Galaxite is a normal spinel, whose crystal structure was reported by Essene and Peacor (1983) and Lucchesi et al. (1997). Structural and spectroscopic data on synthetic MnAl₂O₄ are known as well (Hålenius et al. 2007).

Hercynite—**FeAl**₂**O**₄. The mineral was discovered by Zippe (1839) and named after the type locality (Poběžovice, Bohemian Forest—in Latin *Silva Hercynia*—Czech Republic). Several single-crystal and powder structures of natural hercynite are available in literature (e.g., Larsson et al. 1994; Harrison et al. 1998); the series FeAl₂O₄—FeCr₂O₄ was studied by single-crystal X-ray diffraction and FTIR (Lenaz and Skogby 2013). Recently, Lavina et al. (2009) discussed the intracrystalline cation distribution on two sets of fast-cooled anatectic and slow-cooled metamorphic hercynites.

Jacobsite—MnFe₂O₄. The mineral was first found at the Jakobsberg mine, Värmland, Sweden (Damour 1869) and named jakobsite after the type locality. The name was then changed in jacobsite (e.g., Johannson 1928). Whereas, according to Essene and Peacor (1983), wide *solvi* at metamorphic temperatures separate spinel ferrites (jacobsite, franklinite, magnesioferrite, and magnetite) from spinel aluminate, Beard and Tracy (2002) observed an extensive miscibility along the galaxite-jacobsite join. The crystal chemical role of Mn in spinels has been widely investigated owing to the tendency of Mn to exist in two main

oxidation states, i.e., Mn^{2+} and Mn^{3+} . In jacobsite, this difficulty is enhanced by the equilibrium $Mn^{2+} + Fe^{3+} = Mn^{3+} + Fe^{2+}$ and the occurrence of electron hopping between adjacent sites, making the correct assignment of oxidation states difficult. Single-crystal structure refinements of jacobsite from the type locality confirmed the normal character of jacobsite, with Mn^{2+} preferentially hosted at the tetrahedral site (Lucchesi et al. 1997).

Magnesiochromite—**MgCr₂O₄.** Magnesiochromite is the magnesium analog of chromite. In early literature, this mineral was given the name magnochromite (Bock 1868; Websky 1873) and the currently accepted name was first introduced by Lacroix (1910). Even later, Fisher (1929) suggested an unlikely distinction between magnochromite (the pure Mg end-member) and magnesiochromite (intermediate member along the join MgCr₂O₄–FeCr₂O₄), which is today obsolete. The type locality is Schwarzenberg, Saxony, Germany. Several single-crystal structure refinements of magnesiochromite are available, sometimes hidden under the name "chromite" (e.g., Lenaz et al. 2009).

Magnesiocoulsonite—MgV₂O₄. This mineral was first described from the Pereval marble quarry, southern Baikal region, Russia (Reznitsky et al. 1995) and was named for its relationship with coulsonite, being its magnesium analog. No other occurrences are known so far. The crystal structure of synthetic MgV₂O₄ was refined by Reuter et al. (1983).

Magnesioferrite—**MgFe**₂**O**₄. First discovered at Fosso del Cancherone and in the fumaroles of 1855 eruption of the Monte Somma-Vesuvius volcanic complex, Italy, and described by Rammelsberg (1859) under the name magnoferrite. Its current name was later attributed by Dana (1892). Several studies on the cation ordering in magnesioferrite at high-temperature and highpressure conditions were carried out on synthetic compounds (O'Neill et al. 1992; Antao et al. 2005a, 2005b). The synthetic series MgCr₂O₄–MgFe₂O₄ was studied by Lenaz et al. (2006) and Lenaz and Lughi (2013).

Magnetite—FeFe₂O₄. Magnetite is a very common mineral, used since long time for iron metallurgy, and known under different names (e.g., lodestone); Haidinger (1845) mentioned it with its current name magnetite. The type locality is unknown. It is noteworthy that the very first analytical determination of the crystal structure of a member of the spinel group was carried out using a crystal of magnetite (Nishikawa 1914; Bragg 1915). Since then, several structural studies were carried on (e.g., Fleet 1984; Della Giusta et al. 1987).

Manganochromite—**MnCr₂O₄.** Manganochromite is a very rare mineral species first described from the metamorphosed pyrite deposit of Shepherd Hill (Brukunga quarry), Nairne, Mt. Lofty Ranges, South Australia, Australia, by Graham (1978). It occurs as euhedral grains up to $80 \times 800 \ \mu\text{m}$ at the contact between pyrrhotite and gangue minerals. The name manganochromite was given by analogy with the name magnesiochromite, of which manganochromite is the Mn-analog. At the type locality, Cr is partially replaced by V, showing extensive solid solution with vuorelainenite, as observed by Zakrzewski et al. (1982) at the Sätra mine, Sweden. Crystal structure data on manganochromite are not available; the structure of synthetic MnCr₂O₄ was refined by Raccah et al. (1966).

Qandilite—TiMg₂O₄. Qandilite is a very rare "4-2 spinel", first described from a forsterite skarn in contact with a banded

diorite, in the Dupezeh Mountain, Qala-Dizeh region, Iraq (Al-Hermezi 1985). The mineral has been named after the metamorphic Qandil group in which it occurs. With respect to the ideal end-member formula $TiMg_2O_4$, some Fe^{3+} partially substitutes for Mg^{2+} and Ti^{4+} , and the formula should be better written (Ti,Fe^{3+}) (Mg,Fe^{3+})₂ O_4 . Before the type description, qandilite was found in the Kangerdlugssuaq region, East Greenland, by Gittins et al. (1982); qandilite from Greenland is closer to the end-member composition than that from the type locality, containing 86 mol% $TiMg_2O_4$. Crystal structure data are available only on the synthetic counterpart, $TiMg_2O_4$ (e.g., Wechsler and Von Dreele 1989; Bosi et al. 2014).

Ringwoodite—SiMg₂O₄. Ringwoodite is a silicate spinel and it is the high-pressure isometric polymorph of forsterite and wadsleyite. It was first reported by Binns et al. (1969) from the Tenham meteorite, a chondritic meteorite found in Australia. Ringwoodite occurs as rounded grains up to 100 µm in veinlets cutting the matrix and as pseudomorph after olivine; its origin is probably related to the shock metamorphism. Ringwoodite has been named in honor of Alfred Edward Ringwood (1930–1993), geochemist of the Australian National University, Canberra, Australia. Since the first description, ringwoodite has been reported from several meteorites; the only description of ringwoodite in Earth material was given by Xie et al. (1986) from spinel-lherzolite xenoliths found in the Hannuoba basalt field, Hebei Province, China. Owing to the important petrological role played by ringwoodite in the Earth's transition zone, several crystal structure studies have been performed using synthetic $Si(Mg,Fe)_2O_4$ (e.g., Hazen et al. 1993; Smyth et al. 2003; Ye et al. 2012).

Spinel—MgAl₂O₄. It is the eponymous mineral, known since the antiquity and rewarded for its gemological properties. The first traces of the name date back to the early 17th Century (e.g., de Boodt et al. 1647). The name spinel is likely to come from the Latin *spina* (thorn), in allusion to the pointed shape of the crystals. The name today refers to one of the most common among oxide spinels, the Mg-Al end-member. There is a lot of experimental work on the structural behavior of spinel at different *T* and *P* conditions, carried out mainly on synthetic products; it is noteworthy that the American Mineralogist Crystal Structure Database lists 600 records under the label "spinel".

Trevorite—**NiFe**₂**O**₄. Trevorite is a relatively rare Ni-Fe spinel, first incompletely described by Crosse (1921) from the Bon Accord nickel deposit, South Africa. Then, Walker (1923) gave a full description of this spinel, whose name honors Tudor Gruffydd Trevor (1865–1958), geologist and mining prospector in the Pretoria District. Further data were given by Partridge (1944) and De Waal (1969, 1972). The latter author, studying the nickel minerals from the Bon Accord deposits, described the existence of intermediate members between trevorite and magnetite and gave new data about the former. The crystal structure of synthetic NiFe₂O₄ was refined by Blesa et al. (1993).

Ulvöspinel—**TiFe**₂**O**₄. The mineral was first reported from the Södra Ulvön, Ångermanland, Sweden, by Mogensen (1946) and named after its type locality and its belonging to the oxide spinels. Ramdohr (1953) evidenced that ulvöspinel is a common constituent of titaniferous magnetite, as very thin exsolution lamellae. Crystal structure refinements are available for both natural and synthetic compound (e.g., Stout and Bayliss 1980; Bosi et al. 2009). Ulvöspinel is a "4-2 spinel".

Vuorelainenite—**MnV₂O₄.** First described from the Sätra pyrite mine, Östergötland, Sweden (Zakrzewski et al. 1982), vuorelainenite is a rare Mn-V spinel showing a wide solid solution with manganochromite, as shown by the considerable amount of Cr^{3+} substituting for V³⁺ at the type locality. Several years before the type description, analyses of an oxide spinel corresponding to vuorelainenite, and closer to the end-member composition, were reported from Outokumpu, Finland (Long et al. 1963). The mineral has been named after Yrjö Vuorelainen (b. 1922), exploration geologist with the Outokumpu Company and discoverer of the Outokumpu manganese-vanadium spinel. Crystal structure data on the natural compound are not available, whereas Plumier (1962) refined the structure of synthetic MnV₂O₄.

Zincochromite—ZnCr₂O₄. Zincochromite is a rare member of the spinel group first found at the Srednyaya Padma uraniumvanadium mine, close to Lake Onega, Karelia Republic, Russia (Nesterov and Rumyantseva 1987), where it occurs as very small euhedral crystals (rarely up to 50 μ m), resulting from the breakdown of chromian aegirine. It was named after its composition and the relationship with chromite. Crystal structure data on zincochromite are not available, whereas the structure of synthetic ZnCr₂O₄ was refined by several authors (e.g., O'Neill and Dollase 1994; Levy et al. 2005).

Sulfospinels and selenospinels

Sulfospinels and selenospinels are isostructural with oxide spinels, with the anion represented by sulfur and selenium, respectively. As pointed out by Vaughan and Craig (1978), a very large number of synthetic spinel structure compounds with sulfur, selenium, and also tellurium, have been reported. Actually, 21 natural occurring sulfo- and selenospinels are known to occur (Table 2). Among them, bornhardtite and xingzhongite seem to be questionable. Mineral species are described below in alphabetical order.

Bornhardtite—CoCo₂Se₄. Bornhardtite was described by Ramdohr and Schmitt (1955) from the Trogtal quarry, Harz, Lower Saxony, Germany, as inclusions in clausthalite, together with three other cobalt selenides: trogtalite, hastite, and an unnamed mineral, later named freboldite. Bornhardtite has been named in honor of Wilhelm Bornhardt (1864-1946), German student of ore deposits. The identifications of these cobalt selenides were based exclusively on X-ray powder diffraction data collected on drilled-out material containing a mixture of selenides; in addition, the identifications relied on the paragenesis, hardness, and optical properties. Chemical analyses were not performed and the assumption that the mineral are cobalt selenides were made indirectly, owing to: (1) the occurrence of cobalt in the selenide ore from Trogtal; (2) the similarity between the diffraction pattern to sulfospinels; and (3) to the distinct violet to reddish brown color in reflected light microscopy typical of cobalt minerals. Recently, Keutsch et al. (2009) re-examined one of these phases, hastite, the orthorhombic polymorph of CoSe₂, which was discredited since it corresponded to ferroselite, FeSe2. Consequently, bornhardtite could be considered questionable and further studies are required to confirm its status as a valid mineral species.

	Mineral species	Chemistry	a (Å)	<t-s> (Å)</t-s>	<m-s> (Å)</m-s>	Ref.					
Sulfospinels											
B = Co	Carrollite	CuCo ₂ S ₄	9.464	2.164	2.302	(1)					
	Linnaeite	CoCo ₂ S ₄	9.401	2.198	2.260	(2)					
B = Cr	Cuprokalininite	CuCr ₂ S ₄	9.810	2.260	2.377	(3)					
	Daubréelite	$FeCr_2S_4$	9.976	2.325	2.403	(4)					
	Florensovite	$CuCr_{1.5}Sb_{0.5}S_4$	9.993	2.288	2.429	(5)					
	Kalininite	$ZnCr_2S_4$	9.974	2.325	2.402	(6)					
B = Fe	Greigite	$FeFe_2S_4$	9.876	2.14	2.46	(7)					
$B = \ln \theta$	Cadmoindite	$Cdln_2S_4$	10.797	2.543	2.586	(8)					
	Indite	Feln₂S₄	10.598	2.460	2.558	(8)					
B = Ni	Fletcherite	CuNi ₂ S ₄	9.520	no data	available	(9)					
	Polydymite	NiNi ₂ S ₄	9.457	2.211	2.274	(10)					
	Siegenite	CoNi ₂ S ₄	9.424	2.189	2.273	(11)					
	Violarite	FeNi₂S₄	9.442	2.172	2.289	(12)					
B = PGE	Cuproiridsite	Culr ₂ S ₄	9.847	2.303	2.367	(13)					
	Cuprorhodsite	CuRh₂S₄	9.791	2.272	2.363	(3)					
	Ferrorhodsite	$FeRh_2S_4$	9.890	2.295	2.387	(3)					
	Malanite	$CuPt_2S_4$	9.910	no data	available	(14)					
	Xingzhongite	$Pblr_2S_4$	9.970	no data	available	(15)					
Selenospinels											
	Mineral species	Chemistry	a (Å)	<t-se> (Å)</t-se>	<m-se> (Å)</m-se>	Ref.					
B = Co	Bornhardtite	CoCo ₂ Se ₄	10.2	no data	available	(16)					
	Tyrrellite	CuCo ₂ Se ₄	9.988	2.369	2.384	(17)					
B = Ni	Trüstedtite	NiNi ₂ Se ₄	9.94	no data	available	(18)					
Note: (1) Riedel and Horvath 1973: (2) Lundqvist and Westgren 1938: (3) Riedel											

TABLE 2. Sulfo- and selenospinels: Valid mineral species, ideal chemical compositions, and selected structural data

<u>B = NI</u> Irustedtite NIN₂Se₄ 9.94 no data available (18) Note: (1) Riedel and Horvath 1973; (2) Lundqvist and Westgren 1938; (3) Riedel et al. 1981; (4) Lo Presti and Destro 2008; (5) Warczewski et al. 1997; (6) Wittlinger et al. 1997; (7) Skinner et al. 1964; (8) Hahn and Klingler 1950; (9) Craig and Carpenter 1977; (10) Lundqvist 1947; (11) Huang and Knop 1971; (12) Tenailleau et al. 2006; (13) Furubayashi et al. 1994; (14) Yu 1996; (15) Institute of Geochemistry, Chinese Academy of Science 1981; (16) Ramdohr and Schmitt 1955; (17) Yang et al. 2007; (18) Vuorelainen et al. 1964.

Cadmoindite—**CdIn**₂**S**₄. This mineral was found as octahedral crystals up to 0.15 mm in the high-temperature fumaroles (T = 450-600 °C) of Kudriavy volcano, Kurily, Russia (Chaplygin et al. 2004). X-ray diffraction showed that cadmoindite is the analog of synthetic CdIn₂S₄. Crystal-structure analysis on natural specimen has not been carried out, whereas Hahn and Klinger (1950) solved the crystal structure of synthetic CdIn₂S₄. Cadmoindite is the cadmium analog of indite and the name is after its chemical composition.

Carrollite—CuCo₂S₄. Carrollite was first described by Faber (1852) as a copper-cobalt sulfide with composition $Cu_2Co_2S_4$ on specimens from Finksburg, Carroll County, Maryland, U.S.A. It has been named from the type locality. The status of carrollite as a distinct mineral species from linnaeite was questioned (e.g., Shannon 1926). Meanwhile, Laspeyres (1891) assigned the name "sychnodymite" to a copper-cobalt sulfide from Siegen, Germany. De Jong and Hoog (1928) demonstrated through X-ray data the identity of carrollite and "sychnodymite". Tarr (1935) examining chemical data from literature confirmed the validity of carrollite as mineral species, discrediting "sychnodymite", considered as a Ni-rich variety of carrollite. However, according to Wagner and Cook (1999), no evidence for wide solid solution between carrollite and fletcherite, CuNi₂S₄, is known. Charnock et al. (1990) pointed out the tetrahedral coordination of Cu through extended X-ray absorption fine structure (EXAFS) spectroscopy, whereas X-ray absorption spectroscopy (XAS) demonstrated that the valence state of this element in carrollite is Cu⁺ (Pattrick et al. 2008) and not Cu²⁺ as previously reported (e.g., Charnock et al. 1990).

Cuproiridsite—**CuIr**₂**S**₄. Cuproiridsite was first described by Rudashevsky et al. (1985) from alluvial deposits found in the Aldan shield and in Kamchatka, eastern Russia. It occurs as small inclusions (up to 300 μ m) in isoferroplatinum grains. The crystal structure of cuproiridsite has not been solved, whereas Furubayashi et al. (1994) solved the crystal structure of the synthetic analog. The name is after its chemical composition.

Cuprokalininite—CuCr₂S₄. Cuprokalininite has been recently described by Reznitsky et al. (2011) from the Pereval marble quarry, southern Baikal region, Russia. It occurs as euhedral {111} and {100} crystals, up to 200 µm in size, associated with quartz, Cr-V-bearing tremolite, Cr-V-bearing diopside, mica, calcite, and other rare minerals. Crystal structure was not solved, owing to the ubiquitous {111} twinning of available crystals. Chemical analyses highlighted a significant V enrichment (up to 9.09 wt%, corresponding to 0.526 apfu), as substituent of Cr. Taking into account the physical properties of this compound, two different structural models have been proposed, i.e., $Cu^{+}[Cr^{3+}Cr^{4+}]S_{4}^{2-}$ and $Cu^{2+}Cr_{2}^{3+}S_{4}^{2-}$. At ambient conditions, the former phase is stable, whereas the latter is stable only close to 0 K. According to Reznitsky et al. (2011), no indications of miscibility between kalininite and cuprokalininite have been found. The name underlines that this mineral is the copper analog of kalininite.

Cuprorhodsite—CuRh₂S₄. This mineral was first described by Rudashevsky et al. (1985) from the same occurrence of cuproiridsite, with which cuprorhodsite is strictly associated as micrometric grains in isoferroplatinum. The name is after its chemical composition. Cuprorhodsite forms an extensive solid solution with cuproiridsite and malanite (e.g., Garuti et al. 1995; Barkov et al. 1997). The crystal structure of cuprorhodsite has not been solved, whereas Riedel et al. (1981) studied its synthetic analog.

Daubréelite—FeCr₂S₄. Daubréelite was first described by Smith (1876) from the Coahuila meteorite, Bolsom de Mapimí, Mexico, in association with troilite. Initially, daubréelite was described as a chromium sulfide owing to the small amount of available material and the difficulty of separating it from troilite; two years later, Smith (1878) found more abundant material and was able to chemically separate daubréelite from troilite. Consequently, he succeeded in describing the correct chemical formula of the new mineral. Since then, daubréelite has been found in a large number of metallic meteorites. Owing to its typical occurrence, daubréelite was named after the French scientist Gabriel Auguste Daubrée (1814-1896), who worked extensively with meteorites. Crystal structure was solved by Lundqvist (1943) and since then several crystal structure studies on synthetic FeCr₂S₄ have been performed. EXAFS spectra provide evidences that daubréelite is a normal spinel (Charnock et al. 1990).

Ferrorhodsite—**FeRh**₂**S**₄. Ferrorhodsite is the Fe analog of cuprorhodsite; it has been described by Rudashevsky et al. (1998) from the Chad massif and the Konder alkaline-ultramafic massif, Far-Eastern Region, Russia, as micrometer-sized inclusions (up to $50 \times 70 \ \mu\text{m}^2$) in isoferroplatinum. The name is after its chemical composition and relationship to cuprorhodsite. Crystal structure of natural material has not been solved, whereas the structure of synthetic FeRh₂S₄ was studied by Riedel et al. (1981).

Fletcherite—**CuNi₂S₄**. Fletcherite was found at the Fletcher mine, Reynolds County, Missouri, U.S.A., and described by

Craig and Carpenter (1977). It has been named after the type locality. Fletcherite occurs as crystals ranging in size between 1 and 200 μ m, disseminated in bornite, chalcopyrite, and digenite. Chemical data indicate extensive Ni-Co substitution. Crystal structure was not solved.

Florensovite—**Cu**(**Cr**_{1.5}**Sb**_{0.5})**S**₄. Florensovite was described by Reznitsky et al. (1989) from the Pereval marble quarry, southern Baikal region, Russia. Up to now, this is the only known locality for this species. By analogy with the synthetic counterpart, it is assumed that Cu is monovalent, Cr is trivalent, and Sb is pentavalent. It forms a complete solid solution with kalininite, with a constant Cu:Sb atomic ratio of 2:1, related to the substitution $2Cu^+ + Sb^{5+} = 2Zn^{2+} + Cr^{3+}$. It does not form a solid solution with cuprokalininite (Reznitsky et al. 2011). Florensovite honors Nikolai Aleksandrovich Florensov (1909–1986), Ukrainian geologist, for his contribution to the study of Siberian geology. The crystal structure of synthetic CuCr_{1.5}Sb_{0.5}S₄ has been solved and refined by Warczewski et al. (1997).

Greigite—FeFe₂S₄. The compound Fe₃S₄ was first described by Doss (1912) as melnikovite and confirmed by Polushkina and Sidorenko (1963, 1968) as cubic Fe_3S_4 , identical to the material described by Skinner et al. (1964) under the name greigite. The latter authors reported the occurrence of this sulfospinel from drill cores recovered in Tertiary lacustrine sediments from the Kramer-Four Corners area, San Bernardino County, California, U.S.A. Greigite was named after Joseph Wilson Greig (1895–1977), a mineralogist and physical chemist at the Pennsylvania State University, U.S.A. In 1968, because the name melnikovite was commonly used to designate a wide variety of poorly crystalline iron sulfides, the then CNMMN decided to retain the name greigite (Fleischer 1969). The crystal structure has been reported in the type description (Skinner et al. 1964). Greigite is an inverse spinel and it is the sulfur analog of magnetite (Vaughan and Craig 1985).

Indite—FeIn₂S₄. Indite was described from the Dzhalinda tin deposit, Far-Eastern Region, Russia, as grains <2 mm (rarely up to 0.5 mm) by Genkin and Murav'eva (1963). It has been named after its chemical composition. The crystal structure of indite was not solved but X-ray diffraction data point to its analogy with synthetic FeIn₂S₄, whose crystal structure was reported by Hahn and Klinger (1950).

Kalininite—**ZnCr**₂**S**₄. Kalininite has been described by Reznitsky et al. (1985) in diopside-quartz-calcite rocks of the Slyudyanka complex exploited in the Pereval marble quarry, southern Baikal region, Russia. Up to now, this is the only known locality in which kalininite has been reported. It occurs as irregular slag-like aggregates up to 0.5 mm in garnet and pyroxene, associated with karelianite-eskolaite. It has been named after the mineralogist and petrologist Pavel Vasil'evich Kalinin (1905–1981), investigator of the southern Baikal region. The crystal structure of $ZnCr_2S_4$ has been solved only on synthetic material (i.e., Raccah et al. 1966; Wittlinger et al. 1997).

Linnaeite—CoCo₂S₄. Known since long time with different names (e.g., koboldine, kobaltkies), linnaeite was the first sulfospinel to be recognized as a mineral species (Brault 1746) and it was reported with its current name by Haidinger (1845), in honor of the Swedish taxonomist, botanist, physician, geologist, and zoologist Carl Nilson Linnæus (1707–1778). Its type locality is considered the iron-copper-REE mine of Bastnäs, Västmanland, Sweden. Its crystal structure was solved and refined by Menzer (1926) and, successively, by Lundqvist and Westgren (1938).

Malanite—CuPt₂S₄. Malanite was first described by Yu et al. (1974) during a preliminary study of Chinese platinum minerals occurring in peridotitic rocks but it was not submitted to the IMA approval. In the original description, unit-cell parameter and chemical formula were given as a = 6.03 Å and (Cu,Pt,Ir)S₂, respectively. Peng et al. (1978) re-indexed the powder data on the basis of a cubic cell with a = 10.0 Å, suggesting the chemical formula Cu(Pt,Ir)₂S₄. Yu (1981) re-examined malanite and a mineral previously described as dayingite (Yu et al. 1974), finding the identity between these two phases, with the latter being a cobalt-rich variety of malanite. Finally, malanite was submitted and approved by the Commission on New Minerals and Mineral Names, IMA and described by Yu (1996). The name is after the type locality, the Malan Valley, Chengde Prefecture, Hebei Province, China. In addition to the continuous solid solution with cuproiridsite and cuprorhodsite, malanite can form a solid solution with Ni-Co sulfospinels, i.e., carrollite, CuCo₂S₄, and fletcherite, CuNi₂S₄ (Barkov et al. 1997). Structural data are not available.

Polydymite—NiNi₂S₄. This relatively common nickel sulfospinel was described by Laspeyeres (1876) from the Grünau mine, Siegerland, Germany. The name is after the Greek words πολνς, many, and διδνμος, twin, owing to the widespread twinning shown by its crystals. The crystal structure was solved using synthetic NiNi₂S₄ by Lundqvist (1947).

Siegenite—**CoNi**₂**S**₄. Dana (1850) first reported the name siegenite, after its type occurrence in the Siegen District, Westphalia, Germany; previously, it had been indicated as kobaltnickelkies by Rammelsberg (see Palache et al. 1944). The chemical composition of siegenite lies along the Co-Ni join, between ideal polydymite, NiNi₂S₄, and linnaeite, CoCo₂S₄; natural siegenite can contain minor Cu and Fe (e.g., Zakrzewski 1984). Usually, siegenite lies on the Ni-rich side of the Ni:Co = 1:1 point, along the Co-Ni join (Tarr 1935; Vokes 1967) but Co-rich siegenite has been reported (Petruk et al. 1969). The crystal structure of synthetic CoNi₂S₄ was studied by Huang and Knop (1971).

Trüstedtite—**NiNi₂Se₄.** Trüstedtite was first reported by Vuorelainen et al. (1964) from the Kitka river valley, Kuusamo, Finland, where it occurs in uranium-bearing calcite veins embedded in sills of basaltic rocks. It probably forms a solid solution with polydymite. Trüstedtite was named in honor of Otto Trüstedt (1866–1929), Finnish mining engineer, whose work on prospecting methods lead to the discovery of the Outokumpu ore deposit, Finland. Structural data are not available.

Tyrrellite—CuCo₂Se₄. Tyrrellite was first described by Robinson and Brooker (1952) as an unnamed mineral from Eagle Claims, Beaverlodge Lake area, northern Saskatchewan, Canada. Later, the authors informally named it tyrrellite, in honor of Joseph Burr Tyrrell (1858–1957), geologist of the Geological Survey of Canada who first study the Beaverlodge area. Harris (1970) gave new data of tyrrellite using specimens from the type locality and from a new occurrence at Bukov, Moravia, Czech Republic. The crystal structure of tyrrellite has been solved by Yang et al. (2007). The structural study provided the basis for a redefinition of the chemical formula, Cu(Co,Ni)₂Se₄, rather than the previously suggested $(Cu, Co, Ni)_3Se_4$ (Machatschki and Stradner 1952). Cu is hosted in tetrahedral coordination, whereas Co occurs at the octahedral site.

Violarite—FeNi₂S₄. Clarke and Catlett (1889) described a ferroan variety of polydymite from the Vermilion mine, Sudbury, Ontario, Canada; Lindgren and Davy (1924) recognized the same mineral from the Key West mine, Nevada, U.S.A., and the senior author remarked the differences between this ferroan "polydymite" and polydymite from the German type locality. Consequently, he proposed the institution of the new mineral species violarite; the name is from the Latin violaris, recalling the violet gray color shown by this mineral in polished section. Since then, violarite has been found in several localities worldwide. 57Fe Mössbauer spectroscopy indicates an octahedral coordination of Fe²⁺, although a possible contribution from tetrahedral iron seems to be possible (Vaughan and Craig 1985). This result agrees with the neutron powder diffraction study of iron and nickel ordering in synthetic FeNi₂S₄ performed by Tenailleau et al. (2006), confirming the octahedral coordination of Fe and the inverse type structure of this compound.

Xingzhongite—**PbIr** $_{2}$ **S**₄. The history of xingzhongite is troubled. First described by Yu et al. (1974) from an unknown Chinese locality, xingzhongite was reported as a cubic or pseudocubic minerals with a = 8.72 Å and ideal chemical formula (Ir,Cu,Rh)S. According to Fleischer et al. (1976), the ideal formula could be written as (Cu,Rh,Pb)IrS₂. Peng et al. (1978) re-indexed the cubic cell obtaining a parameter a = 10.10 Å, whereas the Institute of Geochemistry, Chinese Academy of Science (1981) reported new chemical analyses and a cubic cell with a = 9.970 Å, space group $Fd\overline{3}m$. According to Dunn et al. (1984), the new chemical data recalculates, on the basis of 4 S atoms, to $(Pb_{0.37}Cu_{0.35}Fe_{0.17})_{\Sigma=0.89}(Ir_{1.33}Rh_{0.41}Pt_{0.29})_{\Sigma=2.03}S_4$, ideally PbIr₂S₄. In addition, the X-ray powder diffraction patterns collected on the Pb-free and the Pb-bearing phases are different. Consequently, the identity of the Pb-bearing species with the mineral described earlier with the same name is questionable. The confusion about the identity of xingzhongite is confirmed by two studies describing the occurrence of this mineral with the formula proposed by Yu et al. (1974) from New Caledonia (Augé 1988) and the Finero ultrabasic complex, Italy (Garuti et al. 1995). It should be noted that this phase seems to correspond to cuproiridsite.

IMPLICATIONS

In the systematic study of the various mineral classes, the IMA-CNMNC solicited over the years ad-hoc subcommittees to prepare comprehensive reviews on several groups or supergroups of minerals, such as amphiboles, epidotes, zeolites, micas, sulfosalts, etc., aiming at making order on the nomenclature and at establishing general rules for the validity of species within each group. Due to their basic stoichiometry ($AB_2\varphi_4$, with $\varphi = O^{2-}$, S^{2-}), spinels seem to display a quite simple crystal-chemistry; on the contrary, they display a wide chemical variability, with solid-solution series between different end-members. Owing to the outstanding position of spinel-type structure in many branches of Science (e.g., mineralogy, petrology, ore geology, gemology, mineral physics, solid state physics), and due to the lack of any official IMA-CNMNC report on spinels, this short review of the

state-of-the-art of currently valid mineral species could be useful as a base for future crystal-chemical investigations.

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