Revised version #2

An Analysis of the Magnetic Behavior of Olivine and Garnet Substitutional Solid Solutions

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Written on a Mac with Word Version 16.16.2
Date: 01.03.19

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ABSTRACT

The low-temperature magnetic and Néel temperature, $T_N$, properties of four silicate
substitutional solid solutions containing paramagnetic ions are analyzed. The four systems are:
- fayalite-forsterite olivine, Fe$^{2+}$$_2$SiO$_4$-Mg$_2$SiO$_4$, and
- the garnet series, grossular-andradite,
- Ca$_3$(Al$_{1-x}$Fe$^{3+}$$_x$)$_2$Si$_3$O$_{12}$, grossular-spezzartine, (Ca$_{a}$Mn$^{2+}$_{1-x})$_3$Al$_2$Si$_3$O$_{12}$, and
- almandine-spezzartine, (Fe$^{2+}$_{1-x}Mn$^{2+}$_{x})$_3$Al$_2$Si$_3$O$_{12}$. Local magnetic behavior of the transition-metal-bearing
end members is taken from published neutron diffraction results and theoretical calculations. $T_N$
values are from calorimetric heat capacity, $C_P$, and magnetic susceptibility measurements. These
end-members, along with more transition-metal-rich solid solutions, show a paramagnetic to
antiferromagnetic phase transition. It is marked by a $C_P$ λ- anomaly that decreases in temperature
and magnitude with increasing substitution of the diamagnetic component. For olivines, $T_N$
varies between 65 K and 18 K and $T_N$ for the various garnets is less than 12 K. Local magnetic
behavior can involve one or more superexchange interactions mediated through oxygen atoms.
$T_N$ behavior shows a quasi-plateau-like effect for the systems fayalite-forsterite, grossular-
andradite and grossular-spezzartine. More transition-metal-rich crystals show a stronger $T_N$
dependence compared to transition-metal-poor ones. The latter may possibly show
superparamagnetic behavior. (Fe$^{2+}$_{1-x}Mn$^{2+}$_x)$_3$Al$_2$Si$_3$O$_{12}$ garnets show fundamentally different
magnetic behavior. End-member almandine and spezzartine have different and complex
interacting local superexchange mechanisms and intermediate compositions show a double-
exchange magnetic mechanism. For the latter, $T_N$ values show negative deviations from linear
interpolated $T_N$ values between the end members. Double exchange occurs seldomly in oxides,
and this may be the first documentation of this magnetic mechanism in a silicate. $T_N$ behavior
may possibly be used to better understand the nature of macroscopic thermodynamic functions,
$C_P$ and $S^2$, of both end-member and substitutional solid solutions phases.

Keywords: Olivine, garnet, heat capacity, Néel temperature, calorimetry, solid solutions,
transition metals, superexchange, superparamagnetism, double exchange, thermodynamics.
INTRODUCTION

The majority of rock-forming minerals contain transition metals. Iron, either Fe\(^{2+}/3^+\), is the most abundant element in terms of concentration, but Ni\(^{2+}\), Mn\(^{2+/3+}\), Cr\(^{3+}\), and Ti\(^{4+}\) can also be considered major elements in some cases. Transition metals, even in small concentration, can play a key role in determining optical, magnetic and various transport properties in crystals.

Thermodynamic behavior can also be affected by them. Their presence affects large-scale Earth processes as in redox reactions and deep mantle melting, for example. The property of paleomagnetism is based on the ability of a mineral to retain a memory of Earth’s paleogeomagnetic field during crystallization.

At the simplest level, magnetism in minerals results from partially occupied \(d\)-shells of transition-metal ions (minerals with \(f\) electrons can also be magnetic, but for rock-forming minerals these electrons are less important in terms of magnetic behavior). The resulting physical property is a magnetic dipole moment generated by the spin of the electrons. In terms of classical physics, the spin can be described by an electron spinning in either a clockwise or anticlockwise (or spin up and spin down) manner. In quantum terms, this is given by the spin quantum number, where \(M_s = +1/2\) or \(M_s = -1/2\). Magnetic behavior in crystals is determined by the type and strength of the various interactions between the electron spins. These interactions can be of the simple dipole type or more complex ones involving additional intervening atoms (Goodenough 1963; Blundell 2001). All spin interactions are a function of temperature.

Detailed study of the magnetic behavior of crystals in the mineralogical sciences is relatively young (see Parks and Akhtar 1968, for an early work and references therein) and not extensive. In contrast, in physics and material sciences the amount of research made on the magnetic behavior of crystals is enormous. In the late 1940s important theoretical concepts were developed, synthesis experiments on various composition spinel(ferrite)- and garnet-structure crystals were started and investigations on their magnetic properties were made (e.g., Néel 1948; Winkler 1981). Many of these phases contain rare earth elements with partially occupied \(f\)-orbitals, but Fe\(^{2+/3+}\) with \(d\)-electrons is important in many cases.
In contrast, little study has focused on the magnetic properties of rock-forming silicates and especially for substitutional solid solutions. The level of scientific understanding is minimal to nonexistent. In these systems, the electronic configuration of the transition metal(s), its/their structural location and concentration in a crystal are critical, because they together will determine the type of magnetic interaction(s). Fayalite, Fe\(^{2+}\)SiO\(_4\), and fayalite-forsterite, Fe\(^{2+}\)SiO\(_4\)-Mg\(_2\)SiO\(_4\), olivine substitutional solid solutions have received the most study. Fayalite shows a large and relatively high-temperature magnetic transition at about 65 K, but magnetic behavior at lower temperatures down to roughly 20 K is controversial (e.g., Santoro et al. 1966; Robie et al. 1982; Lottermoser et al. 1986; Aronson et al. 2007). With increasing forsterite component in Fe\(^{2+}\)-Mg olivine substitutional solid solutions, the magnetic transition temperature decreases (Dachs et al. 2007; Belley et al. 2009). The common end-member silicate garnets, almandine (Prandl 1971, Murad and Wagner 1987; Anovitz et al. 1993; Dachs et al. 2014b), spessartine (Prandl 1973; Dachs et al. 2009; Lau et al. 2009) and andradite (Murad 1984; Plakhtry et al. 1993; Geiger et al. 2018) have received some experimental study and they undergo a very low temperature (T < 12 K) spin transition. The transition in both silicate structure types of end-member composition is of the paramagnetic-antiferromagnetic type marking a disordered to a long-range ordered spin state. It is defined by the Neel temperature, \(T_N\), which in terms of experimental \(C_p\) measurements is expressed by a \(\lambda\)-anomaly.

We undertook an analysis of the magnetic behavior of the fayalite-forsterite and three garnet binary substitutional solid solutions, namely grossular-andradite, Ca\(_3\)(Fe\(^{3+}\):\(\_x\),Al\(_{1-x}\):\(\_x\))\(_2\)Si\(_3\)O\(_{12}\), grossular-spessartine, (Ca\(_{3-x}\),Mn\(^{2+}\):\(\_x\))\(_3\)Al\(_2\)Si\(_3\)O\(_{12}\), and almandine-spessartine, (Fe\(^{3+}\):\(\_x\),Mn\(^{2+}\):\(\_x\))\(_3\)Al\(_2\)Si\(_3\)O\(_{12}\). A knowledge of \(T_N\) behavior across a given binary join, as determined by low-temperature calorimetry or magnetic susceptibility measurements, together with an understanding of the local magnetic behavior of the one or two paramagnetic end-members, as determined via neutron diffraction and/or calculations, allows the magnetic behavior as a function of composition to be analyzed. This type of study has not been done before.
Furthermore, an analysis of magnetic behavior can help better understand crystal chemical and macroscopic thermodynamic behavior.

**SAMPLES AND LOW-TEMPERATURE CALORIMETRY**

The synthesis conditions or the natural localities for the various crystals of the four binary solid solutions, along with their chemical and physical characterization, have already been described in different publications. The four systems and cited descriptions, discussing the synthesis and characterization measurements, are: i) fayalite-forsterite, Fe$^{2+}_2$SiO$_4$-Mg$_2$SiO$_4$, olivine (von Seckendorff and O’Neill 1993), ii) grossular-andradite, Ca$_3$(Al$_{1-x}$Fe$^{3+}_{3+x}$)$_2$Si$_3$O$_{12}$ (Geiger et al. 2018; Dachs and Geiger 2019), iii) grossular-spessartine, (Ca$_{x}$Mn$^{2+}_{1-x}$)$_3$Al$_2$Si$_3$O$_{12}$ (Geiger 2000; Rodehorst et al. 2004) and iv) almandine-spessartine, (Fe$^{3+}_{x}$Mn$^{2+}_{1-x}$)$_3$Al$_2$Si$_3$O$_{12}$ (Geiger 2000, Geiger and Rossman 1994; Geiger and Feenstra 1997). The various samples are better than about 99% phase pure.

The low-temperature (i.e., 2 or 5 to 300 K) heat capacity, $C_p$, of the various crystals was measured previously with the Physical Properties Measurement System constructed by Quantum Design®. The calorimetric method and measurement set-up have been discussed numerous times (Dachs et al. 2009; 2012; 2014a, b; Geiger and Dachs, 2018; Geiger et al. 2018; Dachs and Geiger 2019) and will not be repeated here.

**EXPERIMENTAL RESULTS**

Low-temperature $C_p$ behavior for synthetic olivines across the Fe$^{2+}_2$SiO$_4$-Mg$_2$SiO$_4$ binary are shown in Dachs et al. (2007). The magnetic transitions and their various $T_N$ values are shown and given, respectively, in this work. The behavior of $T_N$ across the Fe$^{2+}_2$SiO$_4$-Mg$_2$SiO$_4$ binary, as determined by the low-temperature $C_p$ and also by magnetic susceptibility (Belly et al. 2009) measurements, is shown in Figure 1 and Figure 1a, respectively. $T_N$ values are listed in Table 1.
The low-temperature $C_p$ behavior for end-member andradite and solid-solution Ca$_3$(Al$_x$Fe$^{3+}$$_{1-x}$)$_2$Si$_3$O$_{12}$ garnets are shown in Geiger et al. (2018) and Dachs and Geiger (2019).

The low-temperature $C_p$ behavior for spessartine and (Ca$_x$Mn$^{2+}_{1-x}$)Al$_2$Si$_3$O$_{12}$ garnets are shown in Dachs et al. (2009) and Dachs et al. (2014a) and for almandine and (Fe$^{2+}_{x}$Mn$^{2+}_{1-x}$)$_3$Al$_2$Si$_3$O$_{12}$ garnets in Dachs et al. (2012) and Dachs et al. (2014b). The behavior of $T_N$ for all three garnet binaries is displayed in Figure 2. $T_N$ values are listed in Table 1.

Analyses of the $C_p$ results in terms of modeling the magnetic transitions and the determination of $T_N$ are discussed at length in the cited investigations. $T_N$ is given by the peak temperature of the magnetic $\lambda$-anomaly.

DISCUSSION

Heat-capacity measurements and brief theory on magnetism

Thermophysical properties of crystals, including magnetic behavior, can change greatly in the vicinity of the critical temperature of a transition. The subject is broad and complex and cannot be treated here (see Gopal 1966; Grimvall 1986). Suffice it to note that heat-capacity measurements, where $C_p = (dH/dT)_p$ and $H$ is the enthalpy, afford an excellent means of studying $T_N$ and magnetic behavior of crystals (e.g., Stout 1961; Gopal 1966). In the case of most silicates studied to date, magnetic transitions occur below 65 K (i.e., fayalite) and usually at much lower temperatures. Thus, the magnetic interactions are weak, but in some cases they can give rise to larger $C_p(T)$ values than those deriving from atomic vibrations (phonons) at low temperatures. When it is possible to separate the vibrational (phonon or lattice) heat capacity, $C_{ vib}$, from the magnetic heat capacity, $C_{ mag}$, from experimental $C_p$ measurements important information is obtained (e.g., Gopal 1966).

Experimental investigations of different types made on transition-metal-bearing olivines and garnets demonstrate that these two structure types undergo one or two magnetic or magnetic-related transitions at low temperatures. In terms of calorimetry, it is marked by a $\lambda$-
peak or -anomaly (i.e., 2\textsuperscript{nd} order phase transition) that describes the thermophysical changes resulting from the magnetic interactions, whereby disordered electron spins begin to interact locally and order with decreasing temperature. The start of spin ordering (short range) coincides with the onset of the high-temperature flank of the $\lambda$-peak until reaching a completely long-range ordered state at the critical temperature, that is $T_N$.

According to the Heisenberg model for interacting localized spins, the effective magnetic coupling constant, $J_{\text{eff}}$, is related to $T_N$ (by the relationship:

\[
J_{\text{eff}}/k = \frac{3T_N}{2S(S + 1)}
\]

where $k$ is Boltzmann’s constant, $S$ is the total spin and $z$ is the number of nearest neighbor magnetic ions [$z = 2$ (M1) and 4 (M2) for olivine and $z = 4$ (dodecahedral site) or 6 (octahedral site) for garnet]. On the basis of accurate crystal-structure results, the magnetic coupling constant, $J$, for two weakly coupled localized spins $S^A$ and $S^B$ can be obtained from the energy difference between parallel ($S_{\text{max}}$) and antiparallel ($S_{\text{min}}$) alignment of the spins (Zherebetskyy et al. 2012 and references therein). It is given by:

\[
J = -\frac{E(S_{\text{max}}) - E(S_{\text{min}})}{S_{\text{max}}^2 - S_{\text{min}}^2}
\]

where the numerically calculated $E(S)$ is the total energy for the spin state, $S$. Positive values of $J$ correspond to parallel or ferromagnetic and negative values to antiparallel or antiferromagnetic coupling of the two spins $S^A$ and $S^B$.

**Olivine and garnet crystal structures**

**Olivine**

Olivine, $X_2$SiO$_4$, with $X = \text{Fe}^{2+}$ (fayalite) and/or Mg (forsterite), is crystallographically orthorhombic with space group $Pbnn$, and it has 4 formula units per unit cell. The crystal structure is shown in Figure 3. The two crystallographically independent cations sites, excluding Si, are termed M1 and M2. M2, Si, O1 and O2 atoms are located on mirror planes and have $m$
point symmetry. The $M1$ cation is located at the origin of the unit cell and has $-I$ point symmetry, while $O3$ and $O4$ occupy general positions of symmetry $I$. A number of structural and crystal-chemical studies investigated the nature of the long-range Mg-Fe$^{2+}$ distribution over the two $M1$ and $M2$ octahedral sites in Fe$^{2+}$-SiO$_4$-Mg$_2$SiO$_4$ solid solutions. There are contradictory results and interpretations obtained over the years. The careful, recent X-ray diffraction investigation of Heinemann et al. (2007) summarize the situation on order-disorder.

Garnet

The garnet crystal structure $Ia-3d$, general formula $\{X3\}[Y2](Z3)O12$, contains three different and independent cation sites (Menzer 1928; Novak and Gibbs 1971) forming a quasi-framework consisting of rigid corner-sharing ZO$_4$ tetrahedra and YO$_6$ octahedra (Armbruster et al., 1992). The structure is shown in Figure 4a. The $Y$-cations are located at the Wyckoff site $16d$ of point symmetry $-3$. The $X$-cations, located at $24c$ of point symmetry $222$, are coordinated by 8 oxygen atoms in the form of a triangular dodecahedron. All sites allow for the incorporation of various cations with or without unpaired $d$- or $f$-electrons (Winkler, 1981), whereby the major cations for the common silicate garnets ($Z$ = Si of point symmetry $-4$) are $X$ = Ca, Mg, Fe$^{2+}$ and Mn$^{2+}$ and $Y$ = Al, Fe$^{3+}$ and Cr$^{3+}$. Accordingly, magnetic interactions can occur on two different sublattices that can, furthermore, interact between each other leading to varying magnetic behavior depending on the garnet chemistry. The occurrence of solid solutions, which can be extensive, of varying compositions can lead to significant changes in the physical properties of garnet (Geiger 2013).

Magnetic and $T_N$ behavior in olivine and garnet solid solutions: Binary systems with a paramagnetic and diamagnetic end member

$Fe^{2+}$-SiO$_4$-Mg$_2$SiO$_4$ olivines
Paramagnetic fayalite shows a magnetic transition at 65 K as measured experimentally several times (e.g., Santoro et al. 1966; Lottermoser et al. 1986; Robie et al. 1982; Aronson et al. 2007). Müller et al. (1982) investigated the magnetic structure of synthetic fayalite using unpolarized neutron diffraction data recorded at 4.2, 35, and 120 K. The various results show that the electronic and magnetic properties deriving from the two crystallographically independent Fe$^{2+}$ atoms at M1 and M2 are complex. Magnetic interactions occur on the two different sublattices that interact, furthermore, between each other. The ab-initio calculations of Cococcioni et al. (2003) for the ground state of fayalite were interpreted as showing that ferromagnetic spin ordering occurs between edge-sharing octahedra (Fig. 3b, d) and antiferromagnetic ordering occurs between corner-sharing octahedra (Fig. 3c) and both through oxygen-mediated superexchange.

Forsterite is diamagnetic, but all studied forsterite-containing Fe$^{2+}$SiO$_4$-Mg$_2$SiO$_4$ solid solutions show a “$\lambda$-anomaly”. $T_N$ decreases with increasing forsterite component in the olivine as observed via calorimetry (Dachs et al. 2007) and magnetic susceptibility measurements (Belley et al. 2009). This behavior is shown in Figure 1 and supplementary Figure 1a (see data in Table 1). The intensity of the $C_P$ $\lambda$-peak also decreases accordingly. $T_N$ values obtained via magnetic susceptibility measurements on fayalite-rich olivines are in good agreement with those obtained from calorimetry. There are greater differences for Fa$_{50}$Fo$_{50}$ and Fa$_{40}$Fo$_{60}$ compositions. Belley et al. (2009) did not observe a transition in more forsterite-rich olivines. (Note: The errors in $T_N$ are considered to be larger than those in Dachs et al. (2007) - Table 1).

In terms of calorimetric determinations, $T_N$ is 65 K for fayalite and $T_N$ decreases to 18.6 K for composition Fa$_{10}$Fo$_{90}$. $T_N$ behavior across the binary join can be described using two linear segments with a break around composition Fa$_{50}$Fo$_{50}$. One segment is given by the $T_N$ values from Fa$_{100}$ to about Fa$_{50}$Fo$_{50}$, while the other segment describes $T_N$ values from about Fa$_{50}$Fo$_{50}$ to Fa$_{10}$Fo$_{90}$. For the
latter, the change in \( T_N \) is less compositionally dependent. All the \( T_N \) data across the binary can
also be fit by a third-order polynomial (Fig. 1).

\[ Ca_3(Al_{3-x}Fe^{3+}_x)_{12}Si_3O_{12} \text{ garnets} \]

Paramagnetic andradite contains one transition-metal cation per formula unit, namely
Fe\(^{3+}\), and it is located at the 16\( a \) octahedral site (Fig. 4a, b and c). Plakhty et al. (1993) analyzed
the nature of the magnon and magnetic exchange interactions in a natural nearly end-member
andradite containing a small amount of Mn\(^{2+}\) and Al\(^{3+}\), as well as in isostructural synthetic
Ca\(_3Fe^{3+}_{12}Ge_{12}O_{12}\), from inelastic neutron scattering measurements made at 4.2 K. The strongest
interactions derive from Fe\(^{3+}\)\((3\sigma^2)\). These workers concluded that magnetic superexchange
occurred through the \( p_\sigma \) orbitals of intermediate oxygen atoms across octahedral-dodecahedra,
Fe\(^{3+}\)-O-(Ca)-O-Fe\(^{3+}\), bridges (Fig. 4c). Meyer et al. (2010) investigated, further, the local
magnetic coupling mechanisms between Fe\(^{3+}\) atoms in And\(_{100}\) using ab-initio methods. They
proposed that the low-temperature antiferromagnetic transition results from weak
superexchange interactions via both Fe\(^{3+}\)-O-(Si)-O-Fe\(^{3+}\) and Fe\(^{3+}\)-O-(Ca)-O-Fe\(^{3+}\) bridges (Fig.
4b, c).

The two different local interactions may possibly be expressed in the \( C_T \) behavior of end-
member andradite (Geiger et al. 2018). Here, the “\( \lambda \)-peak” appears to show a shoulder on its
low-temperature flank (Fig. 5), which is even more pronounced in terms of entropy behavior at
these low temperatures - as given by \( S(T) = \int (C_T/T) \) \(dT \) (Geiger and Dachs 2018). The shorter
superexchange bridge (i.e., Fe\(^{3+}\)-O-(Si)-O-Fe\(^{3+}\)) should be marked by the higher temperature
maximum intensity of the “\( \lambda \)-peak” at 11.3 (± 0.2) K and the longer and weaker superexchange
interaction (i.e., Fe\(^{3+}\)-O-(Ca)-O-Fe\(^{3+}\)) by the low-temperature shoulder at ~5 K. Modeling of the
experimental \( C_T \) data to obtain, \( C_{mag} \), shows that the high-temperature flank of the “\( \lambda \)-peak” that
extends above 11 K (Fig. 5). Therefore, some degree of spin ordering is expected at these
temperatures. More research is needed to address the precise physical nature of the $\lambda$-peak in andradite.

Grossular is diamagnetic, but all studied andradite-containing Ca$_3$(Al$_x$Fe$^{3+}$)$_{1-x}$Si$_3$O$_{12}$ solid solutions show a “$\lambda$-anomaly”. $T_N$ decreases with increasing grossular component in the garnet from 11.3 K in And$_{100}$ (Murad 1984; Geiger et al. 2018) to about 3 K for the most grossular-rich garnets roughly Gro$_{80}$And$_{20}$ (Figure 2 with $T_N$ values given in Table 1). The intensity of the “$\lambda$-peak” also decreases with increasing grossular component in the garnet (Dachs and Geiger 2019). Both indicate a weakening of the local magnetic interactions. The $T_N$ data across the join can be fit with two linear segments with a break occurring around And$_{50}$Gro$_{50}$ (Fig. 2) or with a third-order polynomial.

$(Ca_x,Mn^{2+}_{1-x})_3Al_2Si_3O_{12}$ garnets

Paramagnetic spessartine contains one transition-metal cation per formula unit, namely Mn$^{2+}$, that is located at the 24c dodecahedral site (Fig. 4a). Prandl (1973) investigated the magnetic structure of synthetic spessartine using neutron powder data. Spessartine shows a $\lambda$-anomaly at $T_N = 6.2$ K (Fig. 5 - Dachs et al. 2009) and magnetic susceptibility measurements give a transition at 7 K (Lau et al. 2009). Short-range spin ordering of Mn$^{2+}$($3d^5$) begins above this temperature.

As stated above, grossular is diamagnetic but all studied spessartine-containing $(Ca_x,Mn^{2+}_{1-x})_3Al_2Si_3O_{12}$ solid solutions show a “$\lambda$-anomaly”. $T_N$ values for spessartine and $(Ca_x,Mn^{2+}_{1-x})_3Al_2Si_3O_{12}$ solid-solution garnets are plotted in Figure 2 (values in Table 1). Starting from Sps$_{100}$ and moving to more grossular-rich garnets, $T_N$ decreases from 6.2 K to about 2.2 K for the Sps$_{50}$Gro$_{50}$ composition. At grossular-rich compositions, $T_N$ shows a plateauing behavior with $T_N \leq 2.0$ K (Table 1). A precise determination of $T_N$ for the most grossular-rich garnets is difficult due to their weak and broad $\lambda$-peaks. Moreover, our $C_p$
measurements can only be made down to 2 K. $T_N$ behavior across the join can, once again, be described using two linear segments or a third-order polynomial.

Magnetic behavior as a function of composition

All the experimental data on olivine show a decreasing and nonlinear behavior in $T_N$ across the Fe$^{2+}$SiO$_4$-Mg$_2$SiO$_4$ join. $T_N$, marking a paramagnetic-antiferromagnetic transition, decreases from Fa$_{100}$ to Fa$_{10}$Fo$_{90}$ with a quasi-plateauing behavior for forsterite-rich compositions. The magnetic structure in the fayalite-rich solid solutions should be governed, as in Fa$_{100}$ (Cococcioni et al. 2003), by superexchange interactions through oxygen among Fe$^{2+}$ cations (Fig. 3b, c and d). A decrease in the intensity of the $\lambda$-peak as a function of composition also demonstrates a weakening of the local magnetic interactions.

Analogous $T_N$ behavior is observed for Ca$_3$(Al$_x$Fe$^{3+}$_{1-x})$_2$Si$_3$O$_{12}$ and (Ca$_x$Mn$^{2+}$_{1-x})$_3$Al$_2$Si$_3$O$_{12}$ garnets and the variation in magnetic properties could be similar to that in olivine. Andradite and spessartine transition to an antiferromagnetic state and this is also considered the case for andradite- and spessartine-rich solid solutions. For both binaries, $T_N$ shows a quasi-plateau-like effect, whereby $T_N$ is more strongly temperature dependent in garnets richer in paramagnetic cations compared to those richer in diamagnetic ones, namely Al$^{3+}$ and Ca$^{2+}$, respectively.

$T_N$ for all three solid-solution binaries appears to exhibit a change in temperature dependence roughly around the 50:50 composition region. Notably, magnetic ordering persists in paramagnetically-dilute solid solutions and in the case of olivine even for the Fe$^{2+}$-poor composition Fa$_{10}$Fo$_{90}$. Superexchange is responsible for magnetic ordering in the transition-metal-bearing end members and as well, we think, for the magnetic-cation-rich compositions. However, it would appear to be difficult for superexchange to persist in compositions richer in the diamagnetic component, because superexchange is a local interaction, decreasing
exponentially in strength with distance. The observed magnetic ordering in diamagnetic-component-rich solutions requires long-range interactions. What are the alternatives?

The first and most obvious one is dipolar interactions between randomly distributed isolated magnetic ions. An estimate of the order of magnitude of the magnetic energy, \( U_{\text{mag}} \), of the dipole interaction between two free Fe\(^{2+} \) cations, for example, with (anti)parallel alignment is given by

\[
U_{\text{mag}} \cdot 10^{-23} \cdot \frac{\mu^2(\text{Fe}^{2+})}{x^3} \approx 1.25 \text{ K} \cdot \frac{\mu^2(\text{Fe}^{2+})}{x^3} \quad (3),
\]

where \( \mu_B = 9.28 \cdot 10^{-24} \text{ A m}^2 \) is the Bohr magneton, \( \mu \) (Fe\(^{2+} \)) = 4.90, the magnetic moment of Fe\(^{2+} \) in units of \( \mu_B \), \( \mu_0 = 4\pi \cdot 10^{-7} \) is the permeability of the vacuum, and \( x \) is the distance in Ångström between the dipoles. Since dipole-dipole interactions vary as \( 1/x^3 \), they are long-range in nature. Although dipolar interactions have been shown to be significant in low-dimensional systems (Panissod and Drillon 2003), a rough estimate demonstrates that this cannot explain the observed magnetic ordering in the magnetically diluted olivine and garnet systems. For instance, in andradite with a lattice constant of 12.05 Å at 100 K (Armbruster and Geiger 1993), the assumption of randomly distributed magnetic Fe\(^{3+} \) ions in And\(_{20}\)Gro\(_{80}\) yields average distances between about 7 and 10 Å. Substituting these values in eqn. (3), estimated \( T_N \) values in the range of 8 to \( 3 \cdot 10^{-2} \text{ K} \) are obtained, i.e. about two orders smaller than the experimental ones. Similar results yield estimates of \( 2.75 \cdot 10^{-2} \text{ K} \) for And\(_{20}\)Gro\(_{80}\) using mean field theory. In the case of olivine, a value of \( 4 \cdot 10^{-2} \text{ K} \) for Fa\(_{10}\)Fo\(_{90}\) is calculated compared with the observed value of 18.6 K (calculations of R.J. Harrison, private communication). From this first-order analysis, it follows that magnetic dipole-dipole interactions cannot provide the dominating mechanism for spin ordering in diamagnetic-rich crystals.

Alternatively, magnetic ordering may occur in the form of superparamagnetism as observed, e.g., in systems of magnetic nanoparticles embedded in non-magnetic matrices (Bedanta and Kleemann 2009). This implies, as the basic assumption, that the distribution of magnetic ions in dilute solid solutions is not random but that clustering is preferred. That is, in
the more traditional sense, where nanoparticle-like magnetic aggregates are embedded in a nonmagnetic “matrix”. In other words, short-range-cation order should be present in the solid solutions. This proposal may get support by the fact that cation clustering is energetically favorable, in a thermodynamic sense, due to local superexchange within a nanoparticle-like aggregate compared to a nonmagnetic one.

In summary, one possible interpretation of all the data is that two different magnetic mechanisms may be operating across the Fe\(^{2+}\)\(_3\)SiO\(_4\)-Mg\(_2\)SiO\(_4\), Ca\(_3\)(Al\(_3\),Fe\(^{3+}\)_1-x)\(_2\)Si\(_2\)O\(_12\) and (Ca\(_x\),Mn\(^{2+}\)_1-x)\(_2\)Al\(_3\)Si\(_3\)O\(_12\) joins. In terms of olivine, Belley et al. (2009) stated that “magnetic properties do not vary linearly with iron content”. It is notable that the observed \(T_N\) behavior is independent of a particular chemical composition or crystal structure. In both the olivine and the two garnet systems, roughly at the 50:50 composition, the nature of the magnetic interactions changes from local superexchange to long-range interactions possibly between magnetic nanoparticle-like aggregates. If this proposal for \(T_N\) behavior is correct, it is the first report of variable magnetic behavior for a silicate solid solution as well as magnetic cation ordering to the best of our knowledge.

Can short-range cation order occur in garnet or olivine solid solutions?

The question of short-range-cation order in silicate solid solutions has been addressed using \(^{27}\)Al and \(^{29}\)Si MAS NMR spectroscopy. It has been proposed to occur in diamagnetic pyrope-grossular garnets, (Mg\(_x\),Ca\(_{1-x}\))\(_3\)Al\(_2\)Si\(_3\)O\(_12\) (Bosenick et al. 1995; 1999; 2002). Indeed, NMR spectroscopy is the best experimental method in terms of addressing this issue, which is by no means trivial. The experimental problem becomes even more challenging in the case of systems containing paramagnetic ions. The experiments involve the measurement of paramagnetically shifted peaks, whose position is far outside the common range of non-paramagnetic chemical shifts. The resonance assignments and their analysis are not always straightforward. The results on various garnet systems appear to be the most well understood (i.e., Palke et al. 2015; Palke and Geiger 2016). Here, at this stage of research, the spectra do not
appear to show any overt or measurable short-range cation order, that is, clustering. The NMR spectra of forsterite-rich olivines are much more complex and little can be said, because the spectra show many paramagnetically shifted resonances of which nearly all cannot be assigned (McCarty et al. 2015; Stebbins 2018).

**Magnetic and $T_N$ behavior in the (Fe$^{2+}$,Mn$^{2+}$)$_3$Al$_2$Si$_3$O$_{12}$ garnet solid solution: A binary system with two paramagnetic end-members**

The third garnet binary under study has two transition metals that can occur locally at the 24c position (Fig. 4a and d). Low-temperature single-crystal neutron (Prandl 1971) and $^{57}$Fe Mössbauer measurements (Murad and Wagner 1987) show that almandine undergoes a spin transition from a paramagnetic to an antiferromagnetic state. A $\lambda$-peak at about 9.2 K was measured via calorimetry (Anovitz et al. 1993 and Dachs et al. 2012), as shown in Figure 5. The local magnetic structure of almandine in the ground state was investigated by density functional cluster calculations (Zherebetskyy et al. 2012). The interactions causing the transition are complex. The spins of the Fe$^{2+}$($3d^6$) ions at 24c of the edge-shared dodecahedra sublattice (i.e., Fe$^{2+}$-O-Fe$^{2+}$ - Fig. 4d) interact ferromagnetically via superexchange involving intermediate oxygen atoms. Two such separate sublattices are present and they interact further through another superexchange involving connecting SiO$_4$ and AlO$_6$ groups via Fe$^{2+}$-O-(Si)-O-Fe$^{2+}$ and Fe$^{2+}$-O-(Al)-O-Fe$^{2+}$ bridges. Macroscopically, the paramagnetic-antiferromagnetic transition results.

The local magnetic interactions for intermediate (Fe$^{2+}$,Mn$^{2+}$)$_3$Al$_2$Si$_3$O$_{12}$ garnets are most interesting, because they are totally unlike the other two garnet solid solutions discussed above. (Fe$^{2+}$,Mn$^{2+}$)$_3$Al$_2$Si$_3$O$_{12}$ garnets show nonlinear and negative $T_N$ behavior across the binary between Sp$_{8100}$ and Alm$_{8100}$ (Fig. 2). There is no plateauing-like behave towards either end member. The high-spin $d$-electron configurations are $(d^7d_{\uparrow})$ for Fe$^{2+}$ and $(d^5)$ for Mn$^{2+}$. If both cations are present in a solid-solution crystal, this may lead to another type of magnetic
interaction known as double exchange. This mechanism was first described by Zener (1951)

between Mn$^{3+}$ and Mn$^{4+}$ in nominal LaMnO$_3$ perovskite, whereby some La$^{3+}$ can be replaced by
divalent Ca, Ba or Sr, which are then charge balanced by Mn$^{4+}$ (i.e., La$^{3+}$Mn$^{3+}$ = [Ca, Ba, Sr]$^{2+}$-
Mn$^{4+}$). Further analysis of the physics behind double exchange was given by Anderson and
Hasegawa (1955) and de Gennes (1960). The mechanism is well known in solid-state physics
and materials science, but it, as best we know, has never been reported in rock-forming
minerals. It may occur in certain garnet solid solutions having two divalent magnetic cations at
24c but with different electronic configurations. For (Fe$^{2+}$,Mn$^{2+}$,$\ldots$)$_3$Al$_2$Si$_3$O$_{12}$ garnets, assuming
parallel alignment for the total spins of both ions, Fe$^{2+}$($d^5$,$d^1$)-Mn$^{2+}$($d^5$) with $M_s$(Fe$^{2+}$) = +2
and $M_s$(Mn$^{2+}$) = +5/2, the single spin-down electron of Fe$^{2+}$ can delocalize towards Mn$^{2+}$,
thereby stabilizing the magnetic state. Indeed, electron delocalization leads to a decrease in
kinetic energy in accordance with the Heisenberg uncertainty principle. This delocalization
cannot occur for antiparallel alignment of spins, that is, Fe$^{2+}$($d^5$,$d^1$)-Mn$^{2+}$($d^5$) with $M_s$(Fe$^{2+}$) =
+2 and $M_s$(Mn$^{2+}$) = -5/2 as being inconsistent with the Pauli exclusion principle. Consequently,
the ferromagnetic and the stronger total antiferromagnetic interaction energy observed in Alm$_{100}$
(T$_N$ = 9.2 K) and Sp$_S$$_{100}$ (T$_N$ = 6.2 K) is weakened in the solid solution. Thus, T$_N$ shows negative
deviations from linearity between both end-member garnets for intermediate compositions (Fig.
2).

If magnetic double exchange does occur in (Fe$^{2+}$,Mn$^{2+}$,$\ldots$)$_3$Al$_2$Si$_3$O$_{12}$ garnets, not only is
the magnetic energy lowered, but also the total energy of the system, albeit very slightly. It
follows that there must be a thermodynamic driving force, again very slight, that maximizes the
number of local Fe$^{2+}$,$\ldots$-Mn$^{2+}$,$\ldots$ groupings (i.e., anticlustering). In other words, there would be
unfavorable energetics against forming almandine- or spessartine-like clusters.

Effect of “impurity” atoms on T$_N$
Some of the minor scatter in $T_N$ values for almandine-spessartine garnets (Geiger and Rossman 1994; Geiger and Feenstra 1997), or any garnet for that matter, may result from small amounts of “extra” cations that are not included in the ideal crystal-chemical formulae. Early indications of this are observable in the $^{57}$Fe Mössbauer spectra of almandine (Murad and Wagner 1987) and inelastic neutron scattering results on andradite (Plakhty et al. 1993). $T_N$ of synthetic almandine can be shifted to slightly lower temperatures by the presence of small amounts of octahedral Fe$^{3+}$ (Dachs et al. 2012). The measurable effect of “extra impurity” atoms in small concentrations on $T_N$ in garnet is apparently confirmed.

This is of note because small concentrations of octahedral Fe$^{3+}$ occur in many synthetic and natural almandine crystals (Murad and Wagner, 1987; Geiger et al. 1988; Quartieri et al. 1993; Woodland et al. 1995). Furthermore, at high pressure there is complete solid solution between almandine and skiaigite, ideally Fe$^{2+}$_3Fe$^{3+}_2$Si$_3$O$_{12}$ (Woodland and O’Neill 1993), and, here, the magnetic interactions can be expected to be highly complex.

Magnetic interactions and transitions: Their effect on macroscopic thermodynamic properties and the role of crystal chemistry

*Compositionally end-member silicates*

Both olivines and garnets are orthosilicates, but they are fundamentally different in terms of crystal structure. Fayalite has considerably stronger magnetic interactions than garnet, by nearly an order of magnitude. Indeed, the magnons associated with the magnetic phase transition in end-member fayalite at 65 K contribute more to $C_p(T)$ than phonons between 0 K and about 70 K (Dachs et al. 2007). The relatively energetic magnons derive from the closed-packed olivine structure in which the Fe$^{2+}$ cations are relatively close to each other in M1 and M2 polyhedra and the cations can interact magnetically in several ways (Fig. 3). The two coordination octahedra have shared edges and corners. In fayalite, magnons contribute significantly to the macroscopic thermodynamic behavior at standard conditions. The standard third-law entropy, $S^o$, of a crystal is given by:
assuming $S^{T=0K} = 0$. For fayalite $S_{mag}(298.15 \text{ K})$ is 26.2 J/(mol·K) and it contributes about 17% to $S^o$ that is equal to 151.4 J/(mol·K) - (Dachs et al. 2007).

In the case of end-member garnet with transition-metal cations just occurring at the octahedral site, superexchange interactions are mediated through diamagnetic SiO$_4$ and/or XOs groups (Fig. 4). Thus, the interactions are very weak and magnons occur at very low energies. Andradite is a case in point. The modelled $S_{mag}(298.15 \text{ K})$ is 28.1 J/(mol·K) and it contributes about 9% to $S^o$ that is 325.0 J/(mol·K) - (Geiger and Dachs, 2018). For garnets with transition-metal cations just at the dodecahedral site, the magnetic interactions appear to be even more subtle and complex. The total magnetic interactions involve diamagnetic SiO$_4$ and AlO$_6$ groups and they do not occur directly between edge-shared dodecahedra (Zhrebetskyy et al. 2012), as might be expected from a first-order crystal-chemical analysis. Thus, the corresponding magnon energies are also weaker than in fayalite. For almandine the modelled $S_{mag}(298.15 \text{ K})$ is 32.1 J/(mol·K) and it contributes roughly 10% to $S^o$, that is 336.7 J/(mol·K) - (Dachs et al. 2012). For spessartine the model $S_{mag}(298.15 \text{ K})$ is about 38 J/(mol·K) and $S^o$ is 335.3 J/(mol·K) - (Dachs et al. 2009), thus making up about 11% of the latter. The relevant equation giving the theoretical $S_{mag}$ value is:

$$S_{mag} = R \ln(2S + 1) \text{ per mole of cation} = 29.79 \text{ J/mol-K}$$

(5),

where $R$ is the gas constant and $(2S + 1)$ is the multiplicity, i.e., the number of electron spin orientations. Only for andradite and fayalite is the agreement between model and theoretical $S_{mag}$ values reasonable or good.

What can be stated, further, in terms of magnetic and $C_p(T)$ and $S(T)$ behavior? Various purely empirical $C_p$ models, such as corresponding states models (Anovitz et al. 1993; Lau et al. 2009), or more “seemingly” rigorous lattice-dynamic-type calculations (Gramaccioli et al. 2003; Gramaccioli and Pilati, 2003; Pilati et al. 1996) including neutron scattering measurements (Mittal et al. 2000) have been undertaken on garnet. Their soundness, especially,
in the former cases is questionable. We have been using the simplified lattice dynamic
formulation of Komada (1986) and Komada and Westrum (1997) to model $C_p,\text{vib}(T)$ and $S_{\text{vib}}(T)$
behavior, where “vib” stands for vibrational, using experimental calorimetric $C_p,\text{col}(T)$ results as
input data. If the two former functions can be modeled properly, $C_p,\text{mag}(T)$ and $S_{\text{mag}}(T)$
contributions can be obtained from the difference in values (e.g., $C_p,\text{mag}(T) = (C_p,\text{col}(T) - C_p,\text{vib}(T))$
- see Dachs et al. 2009, 2012; 2014a, b; Geiger et al. 2018, for more detail). An assumption of
this model is that there are no or very minor phonon-magnon interactions. It turns out in some
cases (i.e., almandine, and spessartine) that the model $S_{\text{mag}}(298.15\,\text{K})$ values are less than those
obtained via (5). One possibility that could explain the discrepancy is that phonon-magnon
coupling is occurring. Research in this direction is needed.

Substitutional solid solution silicates

The results of this investigation may help in yet another area involving thermodynamic
properties. It involves macroscopic thermodynamic mixing behavior, namely $\Delta C_p,\text{mix}(T)$ and
$\Delta S_{\text{mix}}(T)$, for solid solutions containing a transition metal ion or ions (see Dachs et al. 2007,
2014a, b; Dachs and Geiger 2019). In short, a precise determination of $\Delta C_{\text{mix, mag}}(T)$ and
$\Delta S_{\text{mix, mag}}(T)$ behavior, obtained from an application of the Komada and Westrum (1997) model,
can be problematic if they are small in magnitude. However, $T_N$ behavior for a solid solution can
help qualitatively in this question, because it can be measured precisely and it is not in any
respect model dependent. Consider the system olivine (Figure 1). Dachs et al. (2007) argued that
$\Delta S_{\text{mix, mag}}(298.15\,\text{K})$ behavior shows slight negative deviations from ideality across the
Fe$^{2+}$:SiO$_4$-Mg$_2$:SiO$_4$ join (i.e., $\Delta S_{\text{mix, mag}} < 0$). $T_N$ behavior shows as well negative deviations from
linearity (Fig 1) between $\text{Fa}_{100}$ and $\text{Fa}_{10}\text{Fo}_{90}$. It must be noted, on the other hand, that a similar
relationship does not appear to exist for andradite-grossular or spessartine-garnet garnets, where
in both cases $\Delta S_{\text{mix, mag}}(298.15\,\text{K}) = 0$. 

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IMPLICATIONS AND CONCLUSIONS

An understanding of the magnetic behavior of silicates, and especially their solid solutions, in both a solid-state physical and mineralogical context, is in its infancy. Little is known and much research remains to be done. In addition to the results presented above, several notable implications can be drawn from this first investigation on olivine and garnet.

First, we conclude based on our analysis, herein, that the observed $\lambda$-anomaly in the low-temperature $C_p(T)$ results on synthetic uvarovite, Ca$_3$Cr$^{3+}$Si$_3$O$_{12}$, and knorringite, Mg$_3$Cr$^{3+}$Si$_3$O$_{12}$ (Klemme et al., 2005; Wijbrans et al., 2014) is caused by a paramagnetic-antiferromagnetic transition. It must be expected that most, if not all, transition-metal-bearing silicate and germanium garnets will have very low-temperature magnetic spin transitions. This may be true for other silicates as well. A determination of their heat-capacity and magnetic behavior will require measurements down to the lowest possible temperatures. This was not always done in the past and it led to incorrect results (see the case for andradite - Geiger et al., 2018).

Second, other silicate-solid-solution systems with a paramagnetic and diamagnetic end member need to be investigated. It has to be determined, for example, how $T_N$ behaves as a function of composition. The systematics need to be more fully studied so that a deeper scientific understanding can be reached.

Third, it can be proposed that double exchange interactions may occur among other magnetic ions than just between Fe$^{2+}$ and Mn$^{2+}$. In terms of garnet, it may occur, for example, between Fe$^{2+}$ at 24c and Fe$^{3+}$ at 16a in certain garnets. For example, double exchange may possibly occur in certain andradites and almandines, where $C_p$ results show small variations in $T_N$ and $\lambda$-anomaly behavior among different crystals (Geiger et al. 2018; Dachs et al. 2012). Furthermore, several rock-forming silicate systems show an exchange between Fe$^{2+}$ and Mn$^{2+}$ and, here, magnetic double exchange may occur. This goes, for example, for the fayalite-tephroite (Mn$_2$SiO$_4$) join (Burns and Huggins, 1972). Marked exchange of Mn$^{2+}$-Fe$^{2+}$-(Mg)
cations occurs in pyroxenes, amphiboles and micas. In all these silicates, Mn\textsuperscript{2+} and Fe\textsuperscript{2+} can be found in corner- and edge-shared octahedral sites and, thus, d-electron delocalization could be expected. Finally, and almost needless to say, the precise magnetic behavior of many solid-solution silicates, containing two or more different transition-metal cations, may prove to be complex in nature. Their low-temperature $C_p$ and magnetic behavior can be expected to be complicated by virtue of the range of possible chemistries and structural sites. The number of different local-electron-spin interactions is expected to be large.

ACKNOWLEDGEMENTS

E.C. Ferré (Lafayette, Louisiana) kindly supplied the data from the magnetic susceptibility measurements on olivine. This study was supported by a grant to C.A.G. from the Austrian Science Fund (FWF: P 30977-NBL). We thank the two referees, and especially R.J. Harrison (Cambridge, UK), whose keen review encouraged us to consider more fully the possible role of superparamagnetism instead of dipole-dipole interactions in the solid solutions. The editor S. Speziale (Potsdam, Germany) also provided useful remarks on improving the clarity of the manuscript.
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Zener, C. (1951) Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of manganese with perovskite structure. Physical Review. 82, 403-40.

Table 1. Neel temperature, $T_N$, for synthetic olivine and three garnet binary solid solutions as determined by relaxation calorimetry and magnetic susceptibility measurements.

<table>
<thead>
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<th>Olivine</th>
<th>$T_N^a$</th>
<th>$T_N^{b2}$</th>
<th>Garnet*</th>
<th>$T_N$</th>
<th>Garnet$^d$</th>
<th>$T_N$</th>
<th>Garnet§</th>
<th>$T_N$</th>
<th>Garnet¶</th>
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<td>Almandine$_{100}$</td>
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<td>Grossular$_{100}$</td>
<td>-</td>
<td>Grossular$_{100}$</td>
<td>-</td>
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Compositions in $^g$Geiger and Rossman (1994) and $^h$Dachs and Geiger (2019).
Figures

Figure 1. Néel temperature, $T_N$, behavior for fayalite-forsterite, Fe$^{2+}$SiO$_4$-Mg$_2$SiO$_4$, olivines. The solid black points give $T_N$ for each olivine composition (errors in $T_N$ are discussed in the text). The data can be described by two linear segments (black dashed lines) or a third-order order polynomial (solid black line). The blue dashed line connects Fa$_{100}$ and Fa$_{10}$Fe$_{90}$. At the bottom of the figure, values for the excess magnetic entropy of mixing for different composition olivines are given by the red diamonds (Dachs et al. 2007). The solid red line represents a 3$^{rd}$-order polynomial fit to the data. The dashed red line represents ideal magnetic entropy of mixing behavior.

Supplementary Figure la (Appendix I). $T_N$ behavior for Fe$^{2+}$SiO$_4$-Mg$_2$SiO$_4$ olivines given by low-temperature $C_p$ and magnetic susceptibility measurements. Black circles: Dachs et al. (2007) and red circles: Belley et al. (2009).

Figure 2. Néel temperature, $T_N$, behavior for three garnet binary substitutional solid solutions. a.) grossular-andradite - Ca$_3$(Al$_{x}$Fe$^{3+}_{1-x}$)$_2$Si$_2$O$_6$, b.) grossular-spesartine - (Ca$_x$Mn$^{2+}_{1-x}$)$_3$Al$_2$Si$_3$O$_{12}$, and c.) almandine-spesartine - (Fe$^{2+}_{x}$,Mn$^{2+}_{1-x}$)$_3$Al$_2$Si$_3$O$_{12}$. The two dashed lines show linear-segment fits to the respective data. The solid curves represent third-order polynomial fits.

Fig. 3. a.) Polyhedral model of fayalite, Fe$_2$SiO$_4$. The isolated SiO$_4$ tetrahedra are shown in red. The M1 (light brown) and M2 (dark brown) sites contain Fe$^{2+}$ in octahedral coordination. b.) M1 octahedra, forming infinite chains, showing the common O1 (dark green colored “beachballs”) and O2 (middle green colored “beachballs”) anions constituting a shared octahedral edge. c.) M2 octahedra showing corner-sharing O2 oxygens (middle green colored “beachballs”) and unshared O1 (solid middle green spheres) and O3 (solid bright green spheres) oxygens. d.) M1 and M2 octahedral showing common edge-shared O3 (bright green colored “beachballs”) and O2 oxygens (middle green colored “beachballs”).

Figure 4. a.) Polyhedral model of silicate garnet. The SiO$_4$ tetrahedra and AlO$_6$ octahedra share corners, building a quasi-three-dimensional framework. The X cations (yellow spheres) are located in small cavities of triangular dodecahedron coordination. b.) In andradite two Fe$^{3+}$/O$_6$ octahedra with Fe$^{3+}$ given by the medium-colored green spheres and a central SiO$_4$ tetrahedron (Si cation dark green). One local superexchange bridge is given by the green colored cations.
(Meyer et al. 2010) and the oxygen anions by “beachball” spheres via Fe\(^{3+}\)-O-(Si)-O-Fe\(^{3+}\). c.) A second possible superexchange in andradite is given by Fe\(^{3+}\)-O-(Ca - light green)-O-Fe\(^{3+}\) bridges (Meyer et al. 2010). d.) One possible relationship between neighboring edge-sharing XO\(_8\) groups for a given almandine-spessartine solid solution (Fe\(^{2+}\) - dark brown and Mn\(^{2+}\) - light brown). “Normal” ferromagnetic superexchange occurs through oxygen anions Zhrebetskyy et al. (2012). Double exchange occurs through the “beachball”-illustrated oxygens. Note that the relative sizes of the various ions are not correct, but made to make the local magnetic interactions easier to visualize.

Figure 5. \(C_p(T)\)\(_\text{mag}\) behavior for almandine (red), spessartine (green) and andradite (blue) normalized to one transition-metal-cation. The three \(\lambda\)-peaks were obtained through calorimetric measurements (Dachs et al. 2012; Dachs et al. 2009; Geiger et al. 2018). \(T_N\) is measurable to better than ± 0.2 K. Note the \(\lambda\)-peak for andradite and the presence of a weak shoulder on the low-temperature flank. Its origin is discussed in the text.
Figure 1.
Figure 2.
Figure 3a, b, c and d.
Figure 4a, b, c, and d.
Figure 5.
Supplementary Figure 1a.