Spin waves and exchange interactions in the antiferromagnetic garnets with Fe$^{3+}$ in the octahedral sites

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Abstract. The results of an inelastic neutron scattering study of the spin wave spectrum for the garnet $\text{Fe}_3\text{Ca}_3\text{Si}_3\text{O}_{12}(\text{FeSiG})$ are presented. We compare the exchange parameters for this garnet and for the Ge-species ($\text{Fe}_3\text{Ca}_3\text{Ge}_3\text{O}_{12}(\text{FeGeG})$) having the same magnetic structure. We relate the differences found with structural information from powder neutron diffraction. In this way the super exchange paths via $p_z$ orbitals of intermediate oxygen atoms can be identified. We discuss the effect of a small number (3.2(5)%) of Mn$^{2+}$ impurities in the 24c sites. These lead to an effective ferromagnetic exchange between the Fe$^{3+}$ ions and drastically renormalize the average exchange constants. An estimate for the Fe$^{3+}$-Mn$^{2+}$ indirect exchange between a and c sites of 6(1) K is obtained. The exchange parameters for the pure FeSiG are found to be $J_1=1.16(4)$ K, $J_1=0.96(4)$ K and $J_2=-1.24(4)$ K for nearest and next nearest neighbours, respectively. These values apply for a moment of 4.02(4) gB per iron atom as obtained from a structure refinement of powder diffraction data. Finally we present results for FeSiG of a high resolution study of the excitations at the zone centre in an attempt to verify our earlier findings of a quantum spin wave gap for FeGeG. In contrast to the earlier measurements, we could follow the acoustical branch to much lower energies using a time-of-flight spectrometer. We found indications for a crossing of the two low lying spin wave branches, the acoustical one extrapolating to the anisotropy gap of 0.005 THz and the “antiphase” branch extrapolating to the quantum gap of 0.02 THz.

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Introduction

Oxides with the general formula $\{M^{III}\}_2\{M^{II}\}_2(M^{II})_2\text{O}_{12}$ crystallize in the garnet structure which is visualized as an oxygen framework with dodecahedral {c}, octahedral {a} and tetrahedral {d} sites occupied by metal cations [1]. The possibility to fill any sublattice with magnetic ions makes this structure a convenient model system for the studies of magnetic phenomena in insulators. In the well-known garnet $\{Y\}_3\{\text{Fe}^{3+}\}(\text{Fe}^{3+})_2\text{O}_{12}$ (YIG), like in many other oxides, the strong intersublattice superexchange interaction via an intermediate oxygen is responsible for the ferrimagnetic ordering at $T_c=560$ K. Numerous antiferromagnetic structures were found at low temperatures in the garnets with $3d$-ions in just one sublattice [2]. The common feature of comparatively weak interactions in these garnets as well as in a number of other low temperature antiferromagnets is due to the absence of single-oxygen bonds between magnetic ions, the superexchange path involving at least two oxygens. Simple arguments for a prediction of exchange parameters [3] do not hold here. Qualitative estimates [2] in mean field approximation give quite unusual values, but they are not very convincing as the stability conditions are not always satisfied (compare also [5]).

The most complete and direct information on the exchange interactions may be obtained by inelastic neutron scattering on the spin wave excitations. In our previous papers [4, 5] the results of such studies on two antiferromagnetic garnets $\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$ (FeGeG) and $\text{Ca}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$ (CrGeG) were reported. They clearly demonstrate how the exchange interactions depend on the electron configuration of the magnetic ions. Here we present the results of a spin wave investigation for $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ (FeSiG). This garnet is isomorphous to the FeGeG but has different nonmagnetic ions in $d$-sites (Si instead of Ge). This gives a possibility to evaluate the influence of the crystal structure on the exchange parameters.

The specific magnetic structure of FeGeG and the small value of its crystalline magnetic anisotropy allowed us to observe the quantum effect of zero point spin fluctuations – an energy gap in the antiphase spin wave branch due to exchange interaction between the transverse spin components [6]. As FeSiG has the same mag-
Magnetic and crystalline structure of FeSiG and FeGeG

The magnetic structures of both FeSiG and FeGeG are identical. In both cases there are two simple antiferromagnetic subsystems shown in Fig. 1 by circles and squares which are displaced by \((1/4 \ 1/4 \ 1/4)\) [7, 8]. Neither spin direction nor relative orientation of the two spin subsystems can be determined by neutron diffraction but the AFMR data [9, 10] show that the [111] direction is the easy axis. Although this spin structure looks like the second kind of antiferromagnetic ordering in the bcc-lattice [11], the symmetry of exchange interactions is quite different. The point symmetry of the octahedral site is 3 and the orientations of the three-fold axes are indicated in Fig. 1 by the dashed lines. As a consequence the nearest neighbour interactions are described by two exchange parameters instead of one [12]: \(J_1\) along the three-fold axis and \(J_{\parallel\parallel}\) in the other space diagonal directions. The next nearest neighbour interactions are given by one parameter \(J_2\) as for the simple bcc-lattice.

![Fig. 1. Spin arrangement of the Fe\(^{3+}\) ions in two subsystems displaced by \((1/4 \ 1/4 \ 1/4)\): o, c-spin up and down in the first subsystem and m, c-spin up and down in the second one. The dashed lines indicate the three fold axes](image)

The superexchange paths between the nearest and next-nearest neighbours are shown on the garnet structure fragment (Fig. 2) by the dashed lines. For \(J_1\), there are three equivalent pairs of oxygen atoms 11–35, 12–36, 13–34 building the edges of dodecahedra. In this notation the oxygen labelling \(ik\) is composed of the octahedral site number \(i\) and the number of the oxygen atom in octahedron \(k\). Three double-oxygen bonds are involved in the \(J'_1\) interaction, namely the edge of dodecahedron 22–36 and the edges of tetrahedra 22–32, 26–36. The next-nearest neighbours (exchange constant \(J_2\)) are coupled via the edge of tetrahedron 12–21. Although this scheme is rather simplified it justifies the next-nearest neighbours approximation. The bonds for the third neighbours include an additional oxygen-oxygen link and are expected to be at least an order of magnitude weaker.

In the molecular field approximation the antiferromagnetic structure of the second kind is stable if \(\langle J'_1 \rangle, J_2 < 0\) and \(J_2/\langle J'_1 \rangle < 1/3\) with \(\langle J'_1 \rangle = (J_1 + 3J_{\parallel\parallel})/4\). From the \(T_N\) and \(\theta_p\) values one obtains [2] for the FeGeG \(\langle J'_1 \rangle = -0.80\) K, \(J_2 = -0.36\) K, i.e. the stability condition is violated. It is seen from Fig. 1 that in the FeGeG the effective field produced by one subsystem cancels out at every spin of the other and vice versa, i.e. the subsystems are decoupled in a static approximation. In this case it appears to be very important to consider the dynamical interaction of the transverse spin components which produces a coupling of the subsystems.

Sample characterisation

While FeGeG can be grown artificially, FeSiG is a high pressure mineral for which no artificially grown single crystals exist. Therefore a natural crystal of FeSiG (andradite) was used. This crystal was scanned on a \(\gamma\)-diffractometer to find the mosaic distribution over the volume. A part of the crystal with a volume of about 2.5 cm\(^3\) and a mosaicity of 1.5° was cut out to be used in the inelastic neutron scattering experiment. It is known that pure natural garnets are very rare, and one can expect some amount of Mn\(^{2+}\), Mg\(^{2+}\) in \(c\)-positions as well as Al\(^{3+}\), Cr\(^{3+}\), Ti\(^{3+}\) in \(a\)-positions of andradite [13]. As the impurity atoms may modify the moment value and exchange parameters the crystal composition should be carefully analysed. By means of X-ray fluorescent and prompt \(\gamma\)-ray analyses manganese and aluminium were found in the amounts of 0.086(7) and 0.09(2) per formula unit, respectively. No other 3d-metals besides Mn were detected. Then a part of the native crystal was ground for powder neutron diffraction measurements which were carried out on the multicounter diffractometer of PNPI. The oxygen coordinates \(x, y, z\), Debye-Waller factors and occupancies of \(c\) and \(a\) sites with calcium (\(n_c\)) and iron (\(n_i\)) were refined from the diffraction pattern measured at room temperature with the neutron wavelength \(\lambda = 1.38\) Å. As a result of this refinement \(n_c = 0.924(8)\) and \(n_i = 0.954(6)\) were obtained. If \(n_c < 1\) due to manganese and \(n_i < 1\) due to aluminium then one obtains \(c_{\text{Mn}} = 0.042(4)\) and \(c_{\text{Al}} = 0.072(9)\) per one position. Values averaged over the neutron diffraction and element anal-