Magnetic Anisotropy in Natural Malachite and Epidote Single Crystals

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Introduction
Malachite, with a formula Cu₂(OH)₂CO₃, forms in a monoclinic crystal structure (space group P121/a1) [1]. This structure is built up from corrugated copper oxides a-c planes formed with edge and corner-sharing distorted CuO₆ octahedra. Epidote, is a natural mineral in which Fe octahedra form linear chains, separated by oxygen, silicon and aluminium atoms. It adopts the monoclinic symmetry, space group P 2₁/m [2]. Both systems should favor a quasi-one-dimensional magnetism.

Experimental
To test such a prediction we have undertaken a series of magnetic bulk experiments using commercial PPMS-14T and MPMS-5T (both Quantum Design) equipment installed at HZB Berlin and LANL Los Alamos. Epidote was studied in the form of a single crystal with field applied along principal axes. Malachite which was not available in single-crystalline form has been studied with field applied along and perpendicular to needle-like crystals (along and perpendicular to the b-axis) forming mammillary aggregate.

Results and Discussion
The magnetic susceptibility of both systems exhibit a little anisotropy at elevated temperatures that becomes more apparent at low temperatures in the case of malachite (see Fig 1). In malachite it can be described at low temperatures as a sum of a Curie-Weiss dependence presumably due to impurities and a thermally activated susceptibility of the form AT⁻¹³exp(-T/Δ), where Δ represents a spin gap. The best fit to the experimental data below 60 K lead to the spin gap value of 119 K [2]. The Δ value is essentially field independent. The magnetization curves shown in Fig. 1 reveals that there is a tendency towards saturation, for the direction along the needle-like crystallites are the magnetization values lower.

Magnetic susceptibility of epidote can be described within a classical Curie-Weiss law with Fe³⁺ ions in the spin high state and θₚ = -31K for all three directions. However, no magnetic order has been found. The magnetization process along the principal axes does not show any tendency towards saturation. The a axis magnetization curve is somewhat special and can be preliminary interpreted in terms of two-sublattice system with a small anisotropy. In one subsystem moments rotate perpendicular to the applied field at lower fields and at higher fields turn towards the applied field. However, in epidote no stable magnetic moments exist. Possible certain amount of interstitial Fe ions has to be checked.

Conclusions
The ratio Δ/T(μmax) = 1 suggests that malachite cannot be considered as a system consisting of isolated dimmers for which the ratio would be larger. From the high temperature magnetic susceptibility one can on the other hand derive the sum of the intrachain couplings, which is about 200 K. On the basis of similar experiments it has been concluded [2] that malachite exhibits a quantum spin liquid ground state, consistent with its structure including s=1/2 alternating chain with rather low inter-chain couplings. Epidote can be regarded as paramagnet with strong AF interactions. However, the 1D character of the Fe ion distribution prevents the system to order magnetically. The rather special shape of the magnetization curve for the a axis needs further study.

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References