SPECIFIC HEAT OF $GeCo_2O_4$ AND $GeNi_2O_4$: FRUSTRATED SPINELS IN MAGNETIC FIELDS TO 14 T

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Introduction

The frustrated magnetic spinels $GeNi_2O_4$ and $GeCo_2O_4$ were selected for the present investigation because Ni^{2+} has a spin-only ground-state, J = 1, while Co^{2+} has a Kramer's doublet ground-state, J = 1/2, with unquenched orbital angular momentum, which results from splitting of the ^4F [L = 3, S = 3/2] free-ion manifold by crystal electric fields. A goal of the research was to see if magnetic ordering in the spinels is influenced by these different ground-states, *i.e.*, one with spin-only coupling and the other with spin-orbit coupling. Both compounds order antiferromagnetically: $GeNi_2O_4$ has two closely spaced, first-order transitions at Néel temperatures (T_N) of $T_{N1}(0) = 12.08$ and $T_{N2}(0) = 11.43$ K; $GeCo_2O_4$ has a first-order transition at $T_N(0) = 20.62$ K, which is accompanied by a crystallographic transition/distortion from face-centered cubic to tetragonal symmetry.

Experimental

A Physical Properties Measurement System at the Los Alamos National High Field Laboratory was used for specific-heat measurements from 2 to 100 K and 0 to 14 T. Measurements at BYU were from 0.3 to 320 K for zero magnetic field.

Results and Discussion

In zero magnetic field (B), well below $T_N(0)$, the magnetic specific heat (C_m) of $GeCo_2O_4$ can be fitted to a gapped (38.6 K—confirmed by spectroscopy), anisotropic, antiferromagnetic spin-wave expression, which is probably associated with the tetragonal distortion. The magnetic entropy recovered is ~70% of 2Rln2. In fields to 14 T, the $T_N(B)$ shift monotonically to lower temperatures as the anomalies attenuate, broaden, and split in large B, which is consistent with anisotropic antiferromagnetism in a polycrystalline sample. An anomaly is "uncovered" at 9.5 T and above that is probably related to the cubic-to-tetragonal distortion. The spin-wave excitations are modified for B > 0; the gap decreases as B increases. Above $T_N(0)$ the entropies for all B are equal. This demonstrates that there is no "hidden" entropy associated with low-temperature anomalies and/or frustration for B = 0 (at temperatures lower than those investigated—0.3 K) to account for the ~30% discrepancy. Well below $T_{N2}(0)$ C_m for $GeNi_2O_4$ can be fitted to an expression that includes both gapless and gapped excitations (11.0 K—confirmed by spectroscopy). Since $GeNi_2O_4$ remains cubic below T_N, gapless antiferromagnetic spin waves are expected. The gapped excitations might be associated with splitting of the S = 1 manifold into a doublet and a higher-energy singlet. The magnetic entropy recovered is ~57% of the expected 2Rln3. Fields to 14 T monotonically increases the separation of the two anomalies and shifts $T_N(B)$ for both to lower temperatures (T_{N2} more rapidly than T_{N1}), while broadening and attenuating them. The shift of $T_N(B)$ with B is, surprisingly, much smaller than that for $GeCo_2O_4$, which has a $T_N(0)$ approximately twice that of $GeNi_2O_4$. For B > 0 the gapped excitations are modified, *i. e.*, the gap decreases as B increases. There is virtually no change in the isotropic spin waves. The entropy for all B above $T_N(0)$ is the same; there are no hidden anomalies and/or "frustration" entropy below the lowest temperature investigated (~0.3 K) for B = 0 to account for the ~43% "missing" entropy. The entropy deficiency, derived from the specific-heat measurements, for both $GeCo_2O_4$ and $GeNi_2O_4$ is probably related to dynamic, thermally-activated formation of "spin clusters" well above T_N. A possible explanation of the dissimilarity of behavior in magnetic fields below $T_N(B)$ for $GeNi_2O_4$ and $GeCo_2O_4$ is their different magnetic ground-state spins of S = 1 and S = 1/2, respectively. This dissimilarity in behavior has also been observed in the magnetic field- and temperature-dependent magnetization of the two compounds.

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