On the magnetic order of Gd_5Ge_3

J. M. Cadogan,[1] D. H. Ryan,[2,a)] Ya. Mudryk,[3] V. K. Pecharsky,[3] and K. A. Gschneidner, Jr.[3]
[1]*School of Physical, Environmental and Mathematical Sciences, UNSW Canberra at the Australian Defence Force Academy, Canberra, ACT BC 2610, Australia*
[2]*Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec H3A 2T8, Canada*
[3]*Ames Laboratory of the U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2300, USA*

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We have investigated the magnetic structure of Gd_5Ge_3 by neutron powder diffraction down to 3.6 K. This compound presents three events in the heat capacity which we show are related to fundamental changes in the magnetic order. The primary antiferromagnetic ordering occurs at 82(2) K and produces a magnetic cell that is tripled with respect to the underlying orthorhombic crystal cell. The propagation vector is $\mathbf{k_1} = [0\,0\,\frac{1}{3}]$. At 74(2) K, the magnetic order becomes "anti-C" with a propagation vector $k_2 = [1\,0\,0]$. A third change in the magnetic order occurs at 40(2) K, and the new magnetic structure is essentially the "anti-C" structure but with the addition of a tripled magnetic component corresponding to a propagation vector $\mathbf{k_3} = [\frac{1}{3}\,0\,0]$. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4852055]

I. INTRODUCTION

The rare-earth intermetallic tetrelides currently enjoy considerable attention due to their demonstrated potential for use as magnetic refrigerant materials, based on their substantial and tunable magnetocaloric effect.[1,2] Most work has focussed on the Gd-based compounds $Gd_5(Si, Ge)_4$. Quite often, an impurity phase $Gd_5(Si, Ge)_3$ is observed to form a plate-like microstructure in the 5:4 samples, and it has been suggested that this 5:3 phase may in fact play a role in the intrinsic magnetic ordering process of the main 5:4 phase.[3]

The crystal structure in the paramagnetic regime is hexagonal Mn_5Si_3-type $P6_3/mcm$ (#193), and it transforms to an orthorhombic subgroup $Cmcm$ (#63) at the magnetic ordering transition.[4] The magnetic ordering behaviour is extremely complex. Briefly, the primary transition temperature from paramagnetic to antiferromagnetic has been reported to occur over a wide range of temperatures, from a low of 48 K to a high of 80 K, and many of the reported transition temperatures are most likely associated with spin-reorientations or rearrangements of the magnetic order, rather than the primary ordering itself. It is also clear that the purity of the starting materials, particularly the gadolinium, has a pronounced effect on the observed magnetic behaviour.[4]

While neutron diffraction is the best way to study magnetic ordering, the extreme absorption cross-section of natural gadolinium makes this challenging. Hot neutrons have been used by Doerr *et al.*[5] who found quite different propagation vectors for two different samples of Gd_5Ge_3, namely, [0 0 0.4] and [0.3 0.3 0], relative to the hexagonal $P6_3/mcm$ cell, which may reflect the purity of the starting materials, as mentioned above.

One drawback to using hot neutrons for diffraction is that the shorter wavelength (~0.5 Å) compresses the diffraction pattern into the low scattering angle range. The aim of our study was to carry out powder diffraction measurements using a longer neutron wavelength and our large-area flat-plate sample mounting method.[6] Despite the rather noisy diffraction patterns obtained, we can clearly identify three magnetically ordered temperature ranges for Gd_5Ge_3, which are in excellent agreement with the results of heat capacity and magnetization measurements on the same high-purity samples.[4]

II. EXPERIMENTAL METHODS

The Gd_5Ge_3 sample used here is the same as that used in an earlier study[4] and was prepared at the Ames Laboratory by arc-melting stoichiometric mixtures of the pure elements. In particular, the gadolinium purity was at least 99.7 at. % with respect to *all* elements in the periodic table. X-ray powder diffraction was used to verify the structure and phase composition of the sample. Neutron powder diffraction experiments were carried out on the DUALSPEC C2 diffractometer at the NRU reactor, Chalk River Laboratories, Ontario, Canada, using a neutron wavelength of 2.3747(2) Å. Diffraction patterns were obtained over the temperature range of 3.6–100 K, and all patterns were analysed using the Rietveld method and the *FullProf/WinPLOTR* program.[7,8] The scattering length for natural gadolinium is strongly dependent on the neutron energy and has been tabulated by Lynn and Seeger,[9] from which we derived the scattering length coefficient appropriate to our neutron wavelength ($\lambda = 2.3747$ Å, $E = 14.51$ meV), namely, $3.0 - 12.7i$ fm.

III. RESULTS AND DISCUSSION

The temperature dependence of the heat capacity of Gd_5Ge_3 has been published previously by some of us[4] and in Figure 1 we show a section of these data. The heat capacity

a)Author to whom correspondence should be addressed. Electronic mail: dhryan@physics.mcgill.ca.

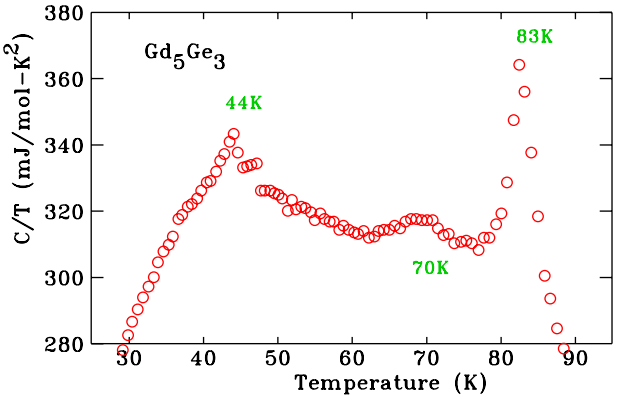

FIG. 1. Temperature dependence of the heat capacity of Gd_5Ge_3 showing the three transitions.[4]

clearly shows three transitions at 83 K, 70 K (broad), and 44 K. The 83 K heat capacity peak marks the primary paramagnetic to antiferromagnetic transition. Here, we will show that all three features are associated with fundamental rearrangements of the magnetic order of the Gd sublattices in Gd_5Ge_3.

In Figure 2, we compare the neutron diffraction patterns obtained at 100 K, 80 K, 55 K, and 3.6 K. The pattern at 100 K comprises the nuclear scattering only, and serves as a reference. Despite the absorption problem, the magnetic ordering of the Gd sublattices is clearly seen and completely dominates the patterns at 55 K and 3.6 K, as evidenced by the large, purely magnetic peak at $2\theta = 9.5°$. This peak indexes as (100) which is not allowed for nuclear or ferromagnetic scattering from the *Cmcm* group for which the scattering condition $h+k=even$ applies. Thus, we may conclude that the magnetic order of the Gd sublattices in Gd_5Ge_3 is antiferromagnetic, consistent with the previous magnetometry work. The dominant magnetic structure corresponds to a propagation vector $\mathbf{k_2} = [1\ 0\ 0]$, leading to "anti-C" order, i.e., moments related by the C-translation $+(\frac{1}{2}\frac{1}{2}0)$ are antiparallel.

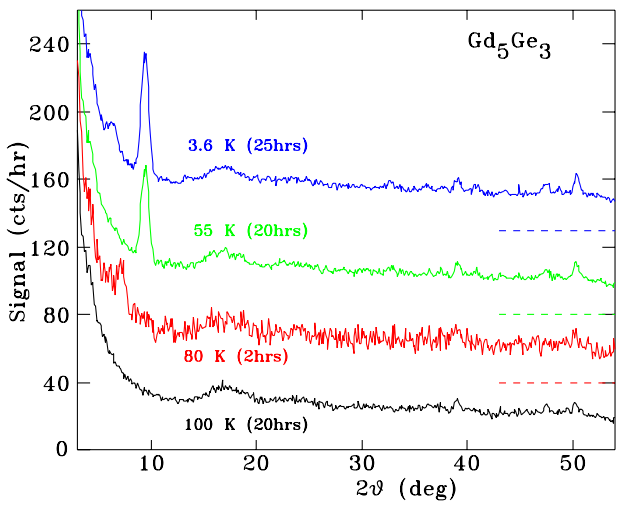

FIG. 2. Neutron powder diffraction patterns of Gd_5Ge_3 obtained at 100 K, 80 K, 55 K, and 3.6 K with a neutron wavelength of 2.3747(2) Å. Some of the patterns have been offset vertically for clarity and the dotted lines show the respective baselines.

While the strong antiferromagnetic (100) peak at $2\theta = 9.5°$ dominates the patterns in Figure 2, a close inspection shows the presence of a weak, purely magnetic peak at $2\theta = 7.5°$ in the 80 K pattern, that can be indexed as $(0\,0\,\frac{1}{3})$, and another weak peak at $2\theta = 6.1°$ in the 3.6 K pattern, close to the $(\frac{2}{3}\,0\,0)$ position. Plotting the temperature dependences of these three magnetic peaks (Figure 3) shows that their onsets correspond to the three events noted in the heat capacity data shown in Figure 1, confirming that all three C_p peaks reflect fundamental changes in the magnetic ordering of Gd_5Ge_3. The primary Néel temperature of 82(2) K is clearly marked by the appearance of the $(0\,0\,\frac{1}{3})$ peak, this is followed by the formation of the "anti-C" antiferromagnetic structure below 74 K. Finally, the $(\frac{2}{3}\,0\,0)$ peak appears near 40 K signalling the final magnetic rearrangement.

A. Magnetic order I: 74 K < T < 83 K

A very weak, purely magnetic peak appears in the diffraction patterns obtained at 80 K and 75 K. It is absent at 85 K and also at 72 K. This matches with the heat capacity data that show primary magnetic ordering at 83 K. This magnetic peak corresponds to $(0\ 0\ 0) + \mathbf{k_1}$ with the propagation vector $\mathbf{k_1} = [0\,0\,\frac{1}{3}]$. The fact that we only observe one rather weak magnetic peak in this temperature range precludes a detailed analysis of the magnetic structure but we can say that the peak represents the primary magnetic ordering of the Gd sublattices.

B. Magnetic order II: 38 K < T < 73 K

Between 75 K and 72 K, the $\mathbf{k_1} = [0\,0\,\frac{1}{3}]$ order gives way to the dominant "anti-C" $\mathbf{k_2} = [1\ 0\ 0]$ order, as evidenced by the strong magnetic (100) peak at $2\theta = 9.5°$, which dominates the patterns obtained below 75 K.

In Figure 4, we show a refinement of the neutron diffraction pattern obtained at 55 K with a propagation vector [1 0 0]. We find the best refinement with the Gd (8e and 8g) moments aligned along the crystallographic b-axis in a

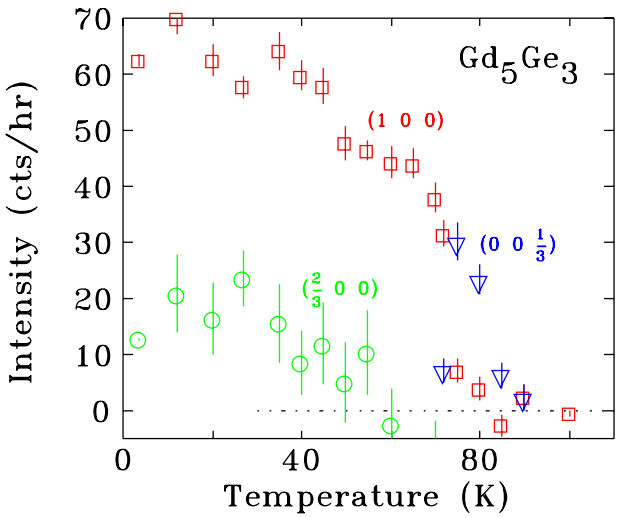

FIG. 3. Temperature dependences of the magnetic intensities of the principal magnetic peaks in the neutron powder diffraction patterns of Gd_5Ge_3. (□) (100) at $2\theta = 9.5°$; (▽) $(0\,0\,\frac{1}{3})$ at $2\theta = 7.5°$; (○) $(\frac{2}{3}\,0\,0)$ at $2\theta = 6.5°$ (note: the $(\frac{2}{3}\,0\,0)$ intensities have been scaled up by a factor of 5).

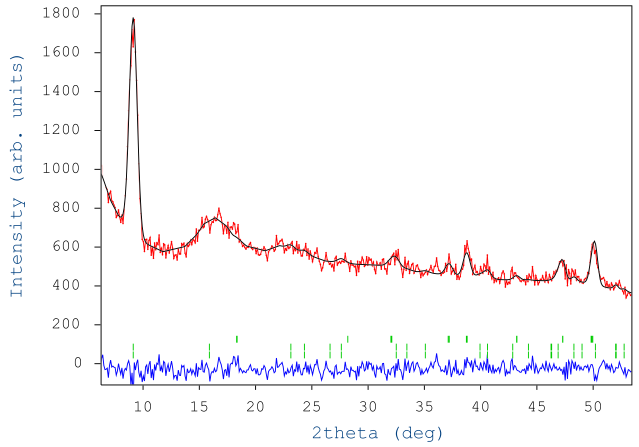

FIG. 4. Refinement of the neutron powder diffraction pattern of Gd_5Ge_3 obtained at 55 K with a neutron wavelength of 2.3747(2) Å. The rows of Bragg markers from top to bottom represent the nuclear and magnetic contributions, respectively.

structure that comprises ferromagnetic sheets with an antiferromagnetic coupling between adjacent sheets. The Gd(4c) moments are midway between adjacent sheets and order antiferromagnetically along the b-axis. The conventional R-factors for this refinement are $R_F = 10.3$, $R_B = 17.4$, and $\chi^2 = 1.33$. The Gd magnetic moments at the three sites were constrained to be equal and the refined Gd magnetic moments are 6.0(3) μ_B. Our observation of b-axis antiferromagnetic order is consistent with the magnetometry work of Tsutaoka *et al.*[10] and Narumi *et al.*[11] who interpreted their findings in terms of planar order in a hexagonal cell, perpendicular to the hexagonal c-axis. This basic ordering mode persists down to 3.6 K, the limit of our measurements.

C. Magnetic order III: T ≤ 38 K

Below about 38 K, a new, weak peak appears at $2\theta = 6.1°$. The position of this new peak, which signals a third magnetic rearrangement, is quite close to $(\frac{2}{3}\,0\,0)$ and suggests a propagation vector of $\mathbf{k_3} = [\frac{1}{3}\,0\,0]$. However, the paucity and quality of the data do not allow a detailed analysis of the ordering arrangement, other than the identification of the propagation vectors. The dominant "anti-C" order is unaffected by this new rearrangement and the tripling along the a-axis is possibly a weak transverse modulation of the dominant b-axis order.

A refinement to the 3.6 K pattern using the magnetic ordering mode found in region II and ignoring the weak peak at $2\theta = 6.1°$, i.e., using $\mathbf{k}_2 = [1\ 0\ 0]$ with the Gd moments aligned along the b-axis, yields Gd moments of 6.6(3) μ_B, almost the "free-ion" value of 7 μ_B, which is consistent with the idea that the new tripling of the magnetic structure represents a weak, probably transverse, modulation.

IV. CONCLUSION

We have used neutron powder diffraction on high-purity Gd_5Ge_3 to show that this compound has a complex magnetic behaviour which involves three magnetically ordered arrangements, each of which is commensurate, with two of the magnetic structures involving a tripling of the unit cell. The observation of three distinct magnetic arrangements is fully consistent with heat capacity work.

ACKNOWLEDGMENTS

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