Lattice specific heat for the intermetallic series RCr_2Si_2 (R = rare earth)

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A combination of Y- and Gd-based RCr_2Si_2 intermetallic compounds is used to establish a reliable set of lattice specific heat data that can be subtracted from data sets for other isostructural compounds to reveal their magnetic and/or crystal field contributions. Broad features associated with low temperature Gd-sublattice transitions of the Gd-based compounds are most likely attributable to amplitude modulation of the ordered Gd moments.

1. Introduction

We report here on a determination of the lattice contribution to the specific heat in intermetallic compounds RCr_2Si_2 (R = Gd - Lu). This work was prompted by earlier specific heat measurements directed at measuring Néel temperatures for the R sub-lattices of $ErCr_2Si_2$ and $TmCr_2Si_2$ [1]. In the case of the $TmCr_2Si_2$ data there was no magnetic transition down to 2 K. However, there was clear evidence for a low temperature Schottky contribution, most likely due to crystal field (CF) splitting of the Tm^{3+} ion's ground state term. In principle, such temperature-dependent specific heat data provide useful additional information that can assist with the CF characterisation. In practice, it is necessary first to strip away, over the full temperature range (2 – 300 K), the electronic and phonon specific heat contributions that are not associated with the 4f shell of the R^{3+} ion. It is the sum of these contributions that we will refer to as the lattice specific heat.

The preferred approach was to record the specific heat for isostructural $LuCr_2Si_2$. The trivalent Lu^{3+} ion's filled 4f-shell is insensitive to CF and magnetic interactions, and Tm and Lu are next-nearest neighbours in the lanthanide series. However, efforts to prepare a suitable single phase specimen of $LuCr_2Si_2$ were unsuccessful. As an alternative "two-pronged" approach, it was decided to record the specific heat for the Y-based compounds YCr_2Si_2 and $Y_{1/2}Lu_{1/2}Cr_2Si_2$ as well as the Gd-based compounds $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$. Y is a common substitute for Lu but it has a significantly smaller atomic mass and the experimental specific heat data need to be rescaled against temperature. For this purpose, we employed the many-Debye method described by Bouvier *et al.* [2], a process that can be justified only for the lower temperature range (less than about a tenth of the Debye temperature). Gd has an atomic mass similar to that of Lu and, because Gd^{3+} (half-filled 4f-shell) is an S-state ion with L = 0, it is insensitive to the CF interaction. However, it is a magnetic ion (S = 7/2) and the Gd-sublattice in $GdCr_2Si_2$ is reported to undergo an antiferromagnetic transition at $T_N \approx 4.3$ K with the Gd moment saturating at 1.6 K [3]. It was anticipated that this would "contaminate" only the lowest temperature range of the lattice specific heat.

2. Experimental details

Polycrystalline specimens of YCr_2Si_2, $Y_{1/2}Lu_{1/2}Cr_2Si_2$, $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$ were prepared from the elements by argon arc melting at least six times to achieve homogeneity. The starting metal purities were 99.99 % for Cr and Si and 99.9 % for the rare

earths. The x-ray powder diffraction (XRD) patterns were recorded using Cu K_α radiation and calibrated against silicon powder. Rietveld analyses were performed using *Rietica* [4]. The specific heat measurements were carried out at Toyoma University, Japan using the relaxation method on a Quantum Design PPMS susceptometer.

3. Results

3.1 X-ray diffraction

The XRD patterns are shown in Fig. 1 for all four specimens.

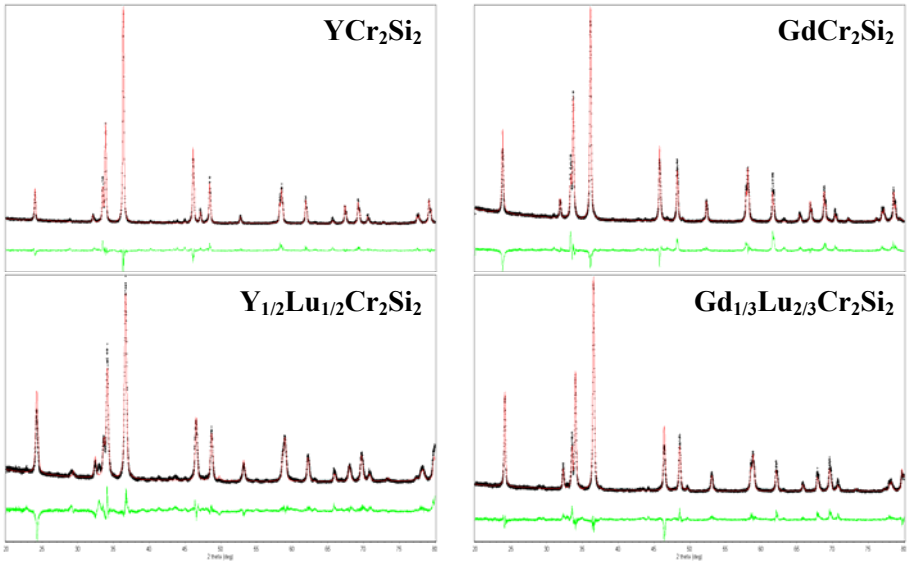

Fig. 1. X-ray diffraction patterns for YCr_2Si_2, $Y_{1/2}Lu_{1/2}Cr_2Si_2$, $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$. The solid lines beneath the plots indicate the difference between the experimental data and the fitted Rietveld theory.

The intermetallic compounds RCr_2Si_2 (R = rare earth) form with the body centred tetragonal, $ThCr_2Si_2$ prototype structure (space group #139, I4/mmm). All four specimens were predominantly single phase with lattice parameters in good agreement with literature values (see Table 1). A small concentration of rare earth oxide was identified in $Y_{1/2}Lu_{1/2}Cr_2Si_2$ but it is unlikely to contribute noticeably to the specific heat signal.

Table 1. Lattice parameters and low temperature specific heat parameters for YCr_2Si_2, $Y_{1/2}Lu_{1/2}Cr_2Si_2$, $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$

Compound	a [nm]	c [nm]	γ [mJ mol^{-1} K^{-2}]	Θ_D [K]
YCr_2Si_2	0.3917(1)	1.0642(1)	6.56(2)	261(1)
	0.39172(4)[(a)]	1.0639(2)[(a)]		
$Y_{1/2}Lu_{1/2}Cr_2Si_2$	0.3893(1)	1.0628(1)	9.91(3)	230(1)
$GdCr_2Si_2$	0.3941(1)	1.0666(1)		
	0.3941(1)	1.0663(3)[(a)]		
$Gd_{1/3}Lu_{2/3}Cr_2Si_2$	0.3891(1)	1.0618(1)		

[(a)] Ref [4]

3.2 Specific heat

Low temperature (2 – 40 K) specific heat data sets for the two Y-based compounds are shown in Fig. 2(a). Also included as solid (YCr_2Si_2) and broken ($Y_{1/2}Lu_{1/2}Cr_2Si_2$) lines are their respective values after rescaling to the case of pure $LuCr_2Si_2$ (according to the many-Debye scaling method [2]). The data sets are seen to converge in a sensible manner with the progression from R = Y through to Lu. As expected, lattice specific heat contribution reduces to $C \approx \gamma T + \beta T^3$ for $T \rightarrow 0$ K (refer to the inset where C/T is evidently a linear function of T^2). The respective derived values of the electronic specific heat coefficient γ and the Debye temperature, $\Theta_D \approx \sqrt[3]{234R/\beta}$, are included in Table 1. The electronic contributions of $\gamma \approx 6$ to 10 mJ mol^{-1} K^{-2} are low compared with those reported for other RT_2Si_2 compounds, ranging from 20 to 25 mJ mol^{-1} K^{-2} [5].

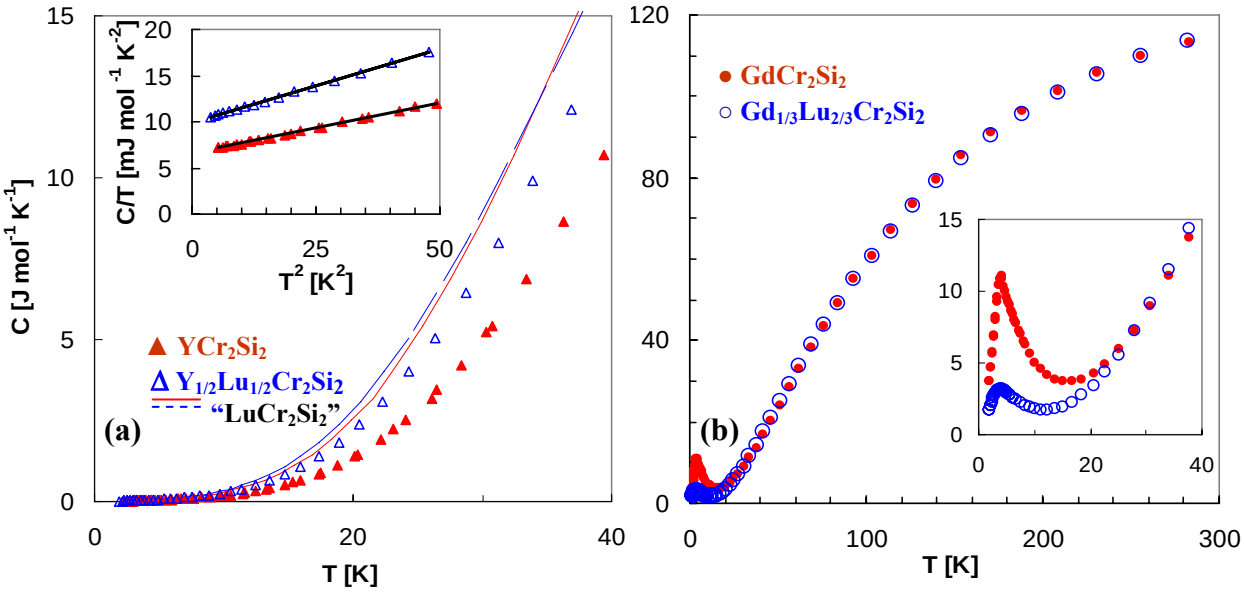

Fig. 2. Specific heat data for (a) YCr_2Si_2 and $Y_{1/2}Lu_{1/2}Cr_2Si_2$ and (b) $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$

The specific heat data for the two Gd-based compounds are shown in Fig. 2(b) for temperatures extending up to room temperature. Both $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$ exhibit broadened (non "lambda"-like) magnetic transition features (expanded views are provided in the inset) that are superimposed on the non-magnetic, lattice contribution below about 30 K. For temperatures beyond 30 K, the two sets of data are in excellent agreement.

3.3 The Gd sublattice magnetic transition

For both Gd-based compounds, the peak value of the specific heat occurs at 4.1 K, only slightly less than the ordering temperature of ≈4.3 K reported by Dommann *et al.* [3]. However, the high temperature limits of the magnetic features extend to well above 4.3 K. This behaviour is reminiscent of specific heat data reported earlier for $GdNi_2Si_2$ and which was attributed to an amplitude modulation of the Gd magnetic moments [2]. Finally, the rescaled YCr_2Si_2 and $Y_{1/2}Lu_{1/2}Cr_2Si_2$ data can be used to strip the lattice specific heat contribution from the specific heat data for $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$ to reveal the respective Gd^{3+} specific heat contributions associated with the magnetic transitions. The resultant data sets are plotted as C_{mag}/T versus T in Fig. 3 and the inset shows magnetic entropy computed as a function of increasing temperature. At 30 K the average entropy contribution is 16.6 J mol^{-1} K^{-1}, which is in reasonable agreement with the expected value of

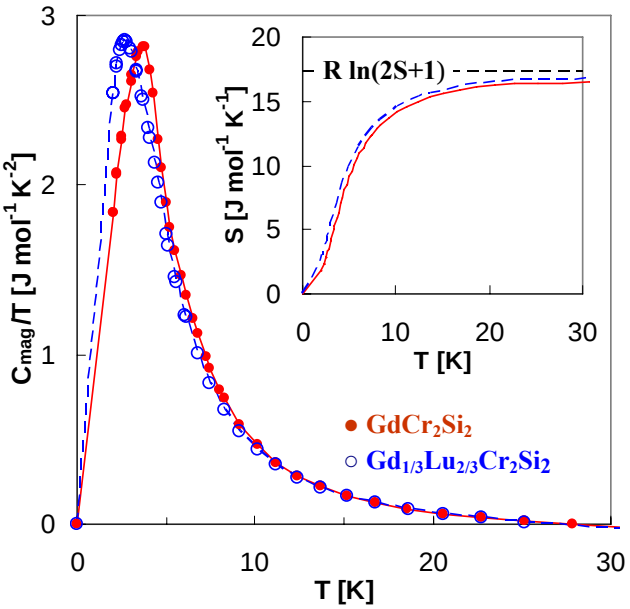

Fig. 3. Specific heat data for the Gd-sublattice magnetic transitions in $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$. The entropy (inset) is calculated via

$$S(T) = \int_0^T (C_{mag}/T')dT'$$

For ease of comparison, all data for $Gd_{1/3}Lu_{2/3}Cr_2Si_2$ are now expressed in terms of mol of atomic Gd rather than mol formula unit.

$R\ln(2S+1) = 17.3$ J mol^{-1} K^{-1} for Gd^{3+} with $S = 7/2$. The deduced entropy curves differ from the earlier result for $GdNi_2Si_2$ [3] in that a much smaller proportion of the full entropy is reached at T_N (47 % compared with 86 %). The quantitative agreement with theory of the entropy determined for the Gd-sublattice magnetic transitions lends support for the validity of the rescaled YCr_2Si_2 and $Y_{1/2}Lu_{1/2}Cr_2Si_2$ specific heat estimates in the lower temperature range of $T \leq 30$ K. It should be mentioned here that the RT_2Si_2 with T = Cr, Mn differ from their counterparts (T = Fe, Co, Ni, Cu) in that the transition metal sublattices order antiferromagnetically at ≈700 K [6]. Based on the success of the rescaled YCr_2Si_2 data, it would seem that the Cr sublattice's magnetic contribution to the specific heat is negligibly small at these lower temperatures.

Conclusion

The important outcome is that the rescaled YCr_2Si_2 and $Y_{1/2}Lu_{1/2}Cr_2Si_2$ specific heat data for $0 < T < 30$ K match relatively seamlessly with the higher temperature data for $GdCr_2Si_2$ and $Gd_{1/3}Lu_{2/3}Cr_2Si_2$. Hence the combined data set will be useful for the purpose of stripping away the lattice contribution from specific heat data recorded for other RCr_2Si_2 with R = heavy rare earth.

Acknowledgements

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References

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