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TiGePt – a study of Friedel differences

The X-ray single-crystal diffraction intensities of the intermetallic compound TiGePt were analysed. These showed beyond doubt that the crystal structure is non-centrosymmetric. The analysis revolves around the resonant-scattering contribution to differences in intensity between Friedel opposites *hkl* and $h\bar{k}\bar{l}$. The following techniques were used: R_{merge} factors on the average (A) and difference (D) of Friedel opposites; statistical estimates of the resonant-scattering contribution to Friedel opposites; plots of $2A_{obs}$ against $2A_{\text{model}}$ and of D_{obs} against D_{model} ; the antisymmetric D-Patterson function. Moreover it was possible to show that a non-standard atomic model was unnecessary to describe TiGePt. Two data sets are compared. That measured with Ag $K\alpha$ radiation at 295 K to a resolution of 1.25 Å⁻¹ is less conclusive than the one measured with Mo $K\alpha$ radiation at 100 K to the lower resolution of 0.93 \AA^{-1} . This result is probably due to the fact that the resonant scattering of Pt is larger for Mo $K\alpha$ than for Ag $K\alpha$ radiation.

1. Introduction

In their study of a structural transformation with negativevolume expansion of the intermetallic compound TiGePt, Ackerbauer et al. (2012) had considerable trouble deciding whether the space group of the low-temperature phase was centrosymmetric or not. Neutron powder diffraction was applied to the problem as the scattering lengths of Ti and Ge are markedly different. Supporting the experimental results with theoretical calculations, these authors were able to show conclusively that the crystal structure of the low-temperature (LT) phase of TiGePt is non-centrosymmetric. Ackerbauer et al. (2012) also studied the crystal structure of the hightemperature phase (> 1158 K) of TiGePt which surprisingly is 10% denser, and has a lower symmetry, than LT-TiGePt. Moreover, Ackerbauer et al. (2012) proposed a mechanistic model for the phase transformation between the low- and high-temperature phases.

In the current paper we have taken an alternative approach to the determination of the symmetry of LT-TiGePt. Singlecrystal X-ray diffraction measurements are used and we deal principally with the analysis of the intensities of Friedel differences. The average and difference of Friedel opposites, both observed and model, are defined as follows: $A(hkl) = \frac{1}{2}[|F(hkl)|^2 + |F(\bar{h}k\bar{l})|^2]$, $D(hkl) = |F(hkl)|^2 - |F(\bar{h}k\bar{l})|^2$. Recent publications of particular relevance to the current paper are Received 16 May 2013 Accepted 2 August 2013



Figure 1

Crystal structure of LT-TiGePt. Ti, Pt and Ge atoms are shown as blue, grey and red spheres, respectively. The shortest Ge-Pt contacts have been drawn.

Flack *et al.* (2011), Parsons *et al.* (2012), Parsons *et al.* (2013) and other papers cited therein.¹

LT-TiGePt crystallizes in the cubic MgAgAs-type structure. The latter can be regarded as a ternary ordered variant of the CaF₂ type. The Ti and Ge atoms are located at the positions of the F atoms, and the Pt atom on the Ca site, occupying one half of the tetrahedral voids. The Ti and Ge atoms have four Pt neighbours in a tetrahedral arrangement. The Pt atom is in a cubic environment, built up of two interpenetrating tetrahedra of Ti and Ge atoms. This structural arrangement is clearly displayed in Fig. 1. Ackerbauer *et al.* (2012) should be consulted for complete information on the crystal structures of TiGePt.

2. Data and structure

Two sets of intensity data were measured from the same crystal specimen and these are labelled Mo and Ag, respectively. The diffraction data set collected in Ackerbauer *et al.* (2012) was used here as the Ag data. Relevant characteristics are given in Table 1, which also includes the values of the resonant-scattering contributions for Ti, Ge and Pt. No

Table 1

Experimental details for LT-TiGePt.

	Data set Mo	Data set Ag		
Chemical formula	TiC	GePt		
$M_{\rm r}$	31	5.58		
Crystal family, space group	Cubic, $F\overline{4}3m$			
Pearson symbol	cl	F12		
Z, formula units per cell		4		
Crystal shape, dimen- sion (µm)	Prism, 20	\times 20 \times 30		
Crystal colour	Metall	ic black		
Crystal data				
$a(\mathbf{A})$	5.9138 (3)	5.9349 (2)		
$V(\text{\AA}^3)$	206.824 (18)	209.05 (2)		
$f'(\mathrm{Ti}), f'(\mathrm{Ge}), f'(\mathrm{Pt})$	0.2776, 0.1547, -1.7033	0.2060, 0.3016, -0.6812		
f''(Ti), f''(Ge), f''(Pt)	0.4457, 1.8001, 8.3905	0.2830, 1.1903, 5.7081		
Data collection				
Diffractometer	Bruker APEX-II	Rigaku R-AXIS Spider		
Radiation	Μο Κα	Ag Kα		
Temperature (K)	100	295		
$\mu (\mathrm{mm}^{-1})$	995.2	477.9		
$T_{\text{max}}/T_{\text{max}}$	1.42	1.23		
$R_{\rm in}$ in $A_{\rm in}$	0.0354	0.0425		
$\sin(\theta)/\lambda$ (Å ⁻¹)	0.03	1 25		
$\sin(\theta)/\lambda_{\rm max}$ (A)	0.95	1.23		
Refinement $P[E ^2 > 2u(E ^2)]$	0.0087	0.031		
$\frac{K[\Gamma > 2u(\Gamma)]}{N_{1}}$	5	0.031		
No. of parameters	5	5		
Reflection count	#Dofloctions [#cots]	#Dofloctions [#sots]		
Management	#Reflections [#sets]	#Reflections [#sets]		
Measured	1/01	804		
Data merged and aver- aged in point group	4 .	3m		
Total	97	207		
Paired acentric [pairs]	80 [40]	172 [86]		
Centric $(0kl, hh0, h00)$	16	28		
Unpaired acentric	1 [1]	7 [7]		
[pairs]				
Data merged and aver-	2	23		
aged in point group				
Total	128	303		
Complete sets of:				
4 m3m general hkl	44 [11]	148 [37]		
2 m3m special 0kl	16 [8]	32 [16]		
2 m3m special bhl	10 [0] 44 [22]	06 [48]		
2 m m special nni2 m m special hhh	++ [22] 12 [6]	20 [40] 14 [7]		
2 m sm special nnn	12 [0]	14 [/] 5 [5]		
1 m3m special hh0	5 [5]	5 [5] 7 [7]		
1 m3m special h00	5 [5]	7 [7]		
Incomplete sets of:				
m3m general hkl	3 [1]	0 [0]		
m3m special hhl	1 [1]	0 [0]		
m3m special hhh	0 [0]	1 [1]		

evidence of twinning was found from the shape of the crystal. A semi-empirical absorption correction using spherical harmonics derived from an assessment of symmetry-equivalent intensities was applied to the intensity data. Fig. 2 shows the distributions of $|F|^2/u(|F|^2)$ against $\sin \theta/\lambda$, and illustrates the differences [absolute values of $|F|^2/u(|F|^2)$ and ranges of $\sin \theta/\lambda$] and similarities [decay of $|F|^2/u(|F|^2)$ and scatter at the same value of $\sin \theta/\lambda$] of the two data sets. $u(|F|^2)$ is the

¹ This study arose in a singular way. The crystal of TiGePt used for structure determination by Ackerbauer et al. (2012) was submitted to the 2011 Zurich School of Crystallography (Linden & Buergi, 2008; http://www.chem.uzh.ch/linden/zsc) by one of the 20 student-participants (S.-V. Ackerbauer) as her project study. Diffraction measurements (Mo $K\alpha$ radiation) were made by the school organizers and the student had to solve and refine the project structure, once two example structures provided by the school had been completed. The intermetallic compound TiGePt is atypical in its chemical composition and symmetry compared with most crystals submitted by the other student participants. At an R value of 1.1%, the study of TiGePt was still producing furrowed brows amongst the ten highly experienced tutors and the student. The values of statistics concerning the fit of Friedel opposites, described below, looked weird. In particular, it was not entirely clear whether the space group was non-centrosymmetric or not, and in the hustle and bustle of the school, there was no time to pursue these problems further. A lively e-mail discussion was undertaken following the school and its results are presented in this paper.

Table 2Atomic coordinates and site occupancies in TiGePt, space group $F\bar{4}3m$.

Atom	Site	Site symmetry	Atom x y z	Fully ordered Ge	Site occupation Ti	Mixed-occupation Ge	Ti
Ti Ge Pt	4a 4b 4c	43m 43m 43m	$\begin{array}{c} 0 \ 0 \ 0 \\ \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2} \\ \frac{1}{4} \ \frac{1}{4} \ \frac{1}{4} \end{array}$	0 1	1 0	$\begin{array}{c} 1-p\\ p\end{array}$	p 1-p

Table 3

TiGePt: R_{merge} values for the 11 (Mo) and 37 (Ag) sets of $m\bar{3}m$ general reflections which have all 4 equivalents hkl, $\bar{h}k\bar{l}$, khl, $\bar{k}h\bar{l}$ in the data set.

R_{merge} (%)	m3m	432	4 3 <i>m</i>	m3
$R_{ F }^{2}$ (Mo)	1.53	1.35	1.05	1.41
$R_{\rm A}$ (Mo)	0.71	0.71	0.71	
$R_{\rm D}$ (Mo)	100	158	63.3	100
$R_{ F }^{2}(Ag)$	4.28	3.62	3.69	3.30
$R_{\rm A}$ (Ag)	2.74	2.74	2.74	
$R_{\rm D}$ (Ag)	100	102	98	100

standard uncertainty of $|F|^2$, see Schwarzenbach *et al.* (1995). The supplementary material² contains relevant data files: (i) hkl, $|F_{obs}|^2$ and $u(|F_{obs}|^2)$ merged and averaged in point group 23 for Mo $K\alpha$ at 100 K and Ag $K\alpha$ at 295 K, (ii) hkl, $|F_{model}|^2$, $|F_{obs}|^2$ and $u(|F_{obs}|^2)$ merged and averaged in point group $\overline{4}3m$ for Mo $K\alpha$ at 100 K and Ag $K\alpha$ at 295 K.

The model of the ordered non-centrosymmetric crystal structure of TiGePt is described in the space group $F\overline{4}3m$ (No. 216), Z = 4, $a \simeq 5.92$ Å, with the atomic positions indicated in Table 2. All atomic coordinates are fixed on special positions and the atomic site symmetries force the harmonic atomic displacement parameters to be isotropic. Study of the phase diagram shows that the LT-TiGePt phase occurs at the equiatomic stoichiometric composition without any homogeneity range (Ackerbauer et al., 2012). One must, however, allow for the partial mixed occupation of different crystallographic sites, in particular the possibility of some Ti atoms occupying the Ge site and some Ge atoms occupying the Ti site. For this case, one finds the appropriate site occupation parameters described in terms of the single parameter p shown in Table 2. A value of p = 1 corresponds to the fully ordered non-centrosymmetric structure. However, for p = 1/2 (with identical atomic displacement parameters on the Ge and Ti sites), the crystal structure has become effectively centrosymmetric, space group $Fm\bar{3}m$ (No. 225), with Pt in site 4b and mixed Ge/Ti occupation of site 8c of that space group. To help in the further analysis of this structure, Appendix A gives the expressions for the average (A) and difference (D) Friedel intensities for the stoichiometric, fully occupied, non-centrosymmetric model structure. The Debye-Waller factors have not been included in these expressions. A least-squares refinement of the Mo data with variable p converges to a value of p close to unity, p = 1.16 (5), $U_{\text{Ti}} = U_{\text{Ge}} = 0.00206$ (6) Å² and $U_{\rm Pt} = 0.00169$ (3) Å².

3. R_{merge} tests

Techniques exploiting the differences in intensities between Friedel opposites and based on the familiar R_{merge} (R_{int}) values which attempt to detect the point group of the crystal are described in this section. These techniques are to be applied at the outset of a structure analysis when no atomic model of the crystal structure is

available. Although full details are given in §3 of Parsons et al. (2012), it is useful to recall briefly the main results of that work. For the chiral (non-centrosymmetric) crystal structure of potassium hydrogen 2R,3R tartrate, it was found that whereas the R_{merge} values on $|F|^2$ weakly indicated the correct point group, the indications of those on D were unequivocally in favour of the chiral crystal structure. Moreover, the study of the centrosymmetric crystal structure of 1-methyl-4-oxotetrahydro-2*H*-imidazol-2-iminium tetrachloro-copper(II) showed almost identical R_{merge} values on either $|F|^2$ or D for all point groups in the Laue class. Most unfortunately, very few such studies have been undertaken and the literature does not provide helpful background information. Further, in studying Table 3 it should be noted that the R_{merge} value on D in a centrosymmetric point group is 100%, not by coincidence, but by definition.

The Laue class of TiGePt was assumed to be $m\bar{3}m$ so, according to Table 2 of Parsons *et al.* (2012), the data files of the observed intensities of TiGePt merged and averaged in point group 23 were obtained. The set of 4 reflections (*hkl*, $\bar{h}k\bar{l}$, *khl*, $kh\bar{l}$) are symmetry-equivalent in the point group $m\bar{3}m$



Figure 2

 $|F|^2/u(|F|^2)$ plots for TiGePt illustrating the features of the data sets used for analysis. Top: Ag data set, bottom: Mo data set.

² Supplementary data for this paper are available from the IUCr electronic archives (Reference: GP5067). Services for accessing these data are described at the back of the journal.

but not so in 23. The numbers of reflections and sets of reflections in the various classes of general and special reflections are given in detail in Table 1 (see the $m\bar{3}m$ entry in Table 1 of Parsons *et al.*, 2012, for the specification of the general and special reflections in $m\bar{3}m$). The number of incomplete sets of reflections is very small so the data sets were considered to be entirely satisfactory for the current analysis.

Table 3 shows the R_{merge} values for the 11 (Mo) and 37 (Ag) sets of $m\bar{3}m$ general reflections with all 4 measurements in the set. For TiGePt the R_{merge} values on the $|F|^2$ seem to indicate that the point group is $\bar{4}3m$ for the Mo data set and $m\bar{3}$ for the Ag data set. However, with the same data and calculating with D, it is very clear for the Mo data set that $\bar{4}3m$ is a better choice than $m\bar{3}$ or $m\bar{3}m$ as the point group of the crystal. The results of the Ag data set are inconclusive. No atomic model was used in coming to this conclusion but an inherent problem with TiGePt is the small number of data available.

4. Friedif

Flack & Bernardinelli (2008) have shown that the product u.Friedif_{stat} usually lies in the range of values between 6 and 10, where *u* is the standard uncertainty of the Flack parameter (Flack, 1983) and Friedifstat is a statistical estimate of the ratio of the root-mean-square Friedel difference to the mean of the Friedel average. Friedifstat is calculated using the chemical composition of the compound and the wavelength of the Xradiation and takes values for TiGePt of 733 with Mo $K\alpha$ radiation and 512 with Ag $K\alpha$ radiation. All Friedif values are given in Table 4. The best least-squares refinement with variable p and independent U_{Ge} and U_{Ti} produced a value of the Flack parameter, x(u), of 0.08 (13) for the Mo data set and -0.04 (24) for the Ag data set. Consequently, for TiGePt we find u.Friedif_{stat} = 95 for Mo and = 123 for Ag, far outside the normal range of values of 6-10. One should seek to understand how this discrepancy might have occurred. It would seem that the values of Friedifstat that have been used are too large. The theoretical derivation of Friedif_{stat} presumes a large number of general acentric Bragg reflections, atoms that are situated only in general positions without any pseudosymmetry, and space group P1. None of these axioms applies to TiGePt. Flack & Shmueli (2007) derived the corresponding formulae for a structure in P1 with a centrosymmetric substructure. These show that with only one atom in a centrosymmetric arrangement in a host of non-centrosymmetrically arranged atoms, the value of Friedif_{stat} is unchanged, whereas for an entirely centrosymmetric structure, Friedif_{stat} becomes zero. The formulae for A_{model} and D_{model} (Appendix A) for the 43m model of TiGePt needed to calculate the Friedif_{model} show that acentric reflections with *hkl* all even have $D_{\text{model}} = 0$ due to all atoms occupying special positions in the unit cell. Using these expressions, which take account of the atomic positions in the crystal structure, one calculates the Friedif_{model} values given in Table 4.

Section 2 of Parsons *et al.* (2012) presents a procedure to determine the status of centrosymmetry in a structure by the

Table 4

Friedif values for TiGePt from the Mo and Ag data sets.

	Mo data set	Ag data set
Friedif _{stat}	733	512
Friedif _{model}	80	51
Friedif _{obs} (all $m\bar{3}m$ general <i>hkl</i>)	18	67
Friedif _{obs} (<i>hkl</i> all even)	15	49
Friedif _{obs} (hkl all odd)	19	83

comparison of Friedif_{stat} with Friedif_{obs} derived from the measured diffraction intensities of acentric reflections. Friedif_{obs} for TiGePt was calculated using the procedure presented by Parsons *et al.* (2012). Values for both data sets are given in Table 4. The standard interpretation of a Friedif_{obs} much smaller than Friedif_{stat} is that the crystal structure is centro-symmetric or non-centrosymmetric but twinned by inversion in a proportion close to 50:50. An alternative interpretation, particularly appropriate to TiGePt, is that a large subset of the intensity data is derived from centrosymmetric projections of the crystal structure or from reflection classes whose Friedel differences happen to be zero as a consequence of special atomic positions. In addition, the average crystal structure of LT-TiGePt may lose its non-centrosymmetric character due to partially mixed occcupations of the Ti and Ge atomic sites.

In all, these approaches show that the diffraction data of TiGePt have a strong centrosymmetric contribution, and leaves the nagging doubt that the crystal structure of TiGePt might indeed be centrosymmetric.

5. AD and Dobs against Dmodel plots

Flack et al. (2011) introduced the D_{obs} against D_{model} plot as a means of validating the intensity data and structural model of a non-centrosymmetric crystal structure. Parsons et al. (2012) have improved this technique in the 2AD plot. Satisfactory plots of D_{obs} against D_{model} and $2A_{obs}$ against $2A_{model}$ show data points distributed about a straight line of slope 1 passing through the origin. Data sets for which the D_{obs} values are dominated by random uncertainties and systematic error show a D_{obs} against D_{model} plot where the data points are arranged along the D_{obs} axis at $D_{model} = 0$. The latter distribution is also shown by centrosymmetric structures. To assess the overall fit of the data, the figures also include $D_{obs} - D_{model}$ and $2A_{obs} - D_{model}$ $2A_{\text{model}}$ values of all reflections, displayed at constant abscissa. These hence show the spread of the deviations of 2A and D, and represent the uncertainties on the individual measurements achieved by the structure refinement.

For TiGePt, the plots of A_{obs} against A_{model} for the two data sets display the required distribution of points about a straight line of slope 1 passing through the origin. The domain of values of $|D_{obs}|$ does not overlap that of $2A_{obs}$ as is usually the case. To make the presentation of the 2AD plot as meaningful and as clear as possible, we chose to plot only the $2A_{obs}$, $2A_{model}$ data points of the 9 reflections with the lowest value of $2A_{obs}$. All of these 9 weak reflections had *hkl* all even with h + k + l = 4n + 2. In this way the overall form both of $D_{obs}D_{model}$ and of the weak $2A_{obs}2A_{model}$ data points can be





2AD plots of TiGePt showing $2A_{obs}$ against $2A_{model}$ for the 9 weakest reflections and D_{obs} against D_{model} for all Friedel pairs. On the left of the plot, $D_{obs} - D_{model}$ and $2A_{obs} - 2A_{model}$ values of all reflections are displayed at constant abscissa. (a) Mo data set; (b) Ag data set. See footnote to §5.

seen. The plots are drawn for the structure refinement with fixed p = 1 and independent variables U_{Ge} and U_{Ti} . The 2AD plots are shown in Fig. 3. For the Mo data set, the fit of $2A_{\text{obs}}$ to $2A_{\text{model}}$ is good even for the 9 weak reflections, whereas that of the Ag data set is much less satisfactory.³

Fig. 4 shows the D_{obs} against D_{model} parts of Fig. 3 magnified. The acentric reflections fall into two distinct classes according to their reflection indices as expected from the formulae for D_{model} given in *Appendix A*. In the first class, *hkl* all even, the data points for the Mo data set in Fig. 4(*a*), are distributed along the line $D_{model} = 0$ as though they were

centric reflections. In the second class, *hkl* all odd, with some imagination, one could say that the data points follow the ideal line of slope 1 passing through the origin. The basis for this interpretation is that a very large proportion of the data points lie in the first and third quadrants. The spread of the hkl all odd reflections is very wide. The domain of $|D_{obs}|$ values in the two classes is approximately the same suggesting that the same random uncertainties and systematic errors affect both classes. In the *hkl* all odd class, the domain of $|D_{obs}|$ values is approximately twice that of $|D_{model}|$ indicating the presence of systematic errors in these intensity data. For the Ag data set in Fig. 4(b), one sees no fit between D_{obs} and D_{model} , the range of $|D_{\text{model}}|$ values being much smaller than that of $|D_{\text{obs}}|$. R values are given in Table 5. For comparison the lowest $R_{\rm D}$ value that we have found to date in other studies is 29% (Flack, 2013). The D_{obs} against D_{model} plot from a refinement with p = 1/2



Figure 4

 $D_{\rm obs}$ against $D_{\rm model}$ of TiGePt. (a) Mo data set; (b) Ag data set. See footnote to §5.

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³ It is arbitrary whether the $D_{obs}(hkl), D_{model}(hkl)$ data point is plotted as $D_{obs}(hkl), D_{model}(hkl)$ or as $D_{obs}(hkl), D_{model}(hkl) = -D_{obs}(hkl), -D_{model}(hkl)$. Indeed both points could be plotted. In Figs. 3 and 4, just one point corresponding to hkl with all positive integers has been plotted.

Table 5
<i>R</i> values for the Mo and Ag data sets of TiGePt.

R values in %	Mo data set	Ag data set
RA	1.13	4.53
R _{Aweak}	1.72	27.7
$R_{\rm D}$ all acentric pairs	76.8	109
$R_{\rm D}$ acentric pairs with <i>hkl</i> all even	100	100
$R_{\rm D}$ acentric pairs with <i>hkl</i> all odd	63.6	115

and independent variables U(0,0,0) and $U(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ looks similar to Fig. 4(*a*) with like *R* values, whereas with $p = \frac{1}{2}$ and $U(0,0,0) = U(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, all reflections have $D_{\text{model}} = 0$ and the structure is centrosymmetric.

In a similar way to the results of §4, the $D_{\rm obs}$ against $D_{\rm model}$ plots do not contain convincing evidence that the structure is really non-centrosymmetric. Changes in the value of p, $U_{\rm Ge}$ and $U_{\rm Ti}$ can drastically modify the appearance of the plot to the point of making it like that of a centrosymmetric crystal.

6. Necessity of a non-standard model

In the intensity data of TiGePt, there are sets of reflections of identical value of $h^2 + k^2 + l^2$, e.g. for $h^2 + k^2 + l^2 = 99$ there are the following three reflections: 339, 177 and 557. In the expressions for A and D of the standard model given in *Appendix A*, the reflections in these sets have identical values of A_{model} and $|D_{\text{model}}|$. Any departure in the corresponding observed values from this equality indicates that the real crystal structure deviates from the standard model by way of either complex static atomic displacements, or anharmonic thermal motion or non-spherical atomic electron density. Despite the small number of such sets of reflections we have nevertheless analysed the corresponding observed values. The R_{merge} evaluates to 0.83% (Mo) and 3.13% (Ag). These values



Figure 5

 A_{obs} - and D_{obs} -Patterson maps of TiGePt along the line [$u \ u \ u$]. Mo data set.

Table	6		
r		 •	41

ļ	n	tera	tomic	vectors	ın	the	structure	ot	TiGel	Pt.

Vector	Atom pairs
$ \begin{bmatrix} 0 & 0 & 0 \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ -\frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{bmatrix} $	$\begin{array}{l} Ti \rightarrow Ti, \ Ge \rightarrow Ge, \ Pt \rightarrow Pt \\ Ge \rightarrow Pt, \ Pt \rightarrow Ti \\ Pt \rightarrow Ge, \ Ti \rightarrow Pt \\ Ti \rightarrow Ge, \ Ge \rightarrow Ti \end{array}$

are slightly less than the R_{int} of each whole data set and indicate that there is no need to extend the model beyond the standard one.

7. A- and D-Patterson functions

Background information on the A- and D-Patterson functions is given in §6 of Flack et al. (2011). Suffice it to say that both show the positions of interatomic vectors in the crystal structure. The A-Patterson function is centrosymmetric, it is calculated with the average intensity of Friedel opposites (hkl and hkl) and it has peaks with a height determined essentially by $Z_i Z_i$, where Z_i is the atomic number of atom *i*. Consequently one sees all interatomic vectors in an A-Patterson map. The D-Patterson function is antisymmetric, it is calculated with the difference intensity of Friedel opposites and it has peaks with a height determined by $(f_i f''_i - f_j f''_i)$ where f_i and f''_i are the real and imaginary components of the atomic scattering factor of atom *i*. Consequently, one only sees interatomic vectors between atoms of different chemical elements in a D-Patterson map. The value of a D-Patterson function of a centrosymmetric structure is zero everywhere.

The coordinates of the atoms in the structure of TiGePt given in Table 2 imply the interatomic vectors given in Table 6. All of them appear along $[u \ u \ u]$ and consequently the A- and D-Patterson functions have been calculated only along this line.

Fig. 5 shows the A_{obs} - and D_{obs} -Patterson functions of TiGePt along the line $[u \ u \ u]$ for the Mo data set. The A_{obs} -Patterson map shows large peaks at u = 0.0, corresponding to the Ge \rightarrow Ge, Ti \rightarrow Ti and Pt \rightarrow Pt self-vectors; at u = 0.25, corresponding to the Pt \rightarrow Ge and Pt \rightarrow Ti vectors; and at u =0.5, corresponding to the Ti \rightarrow Ge vectors, see Table 6. In the intermediate regions, the A_{obs} -Patterson map is close to the background level of zero. One notes that the D_{obs} -Patterson map is also close to zero on the scale of the A_{obs} -Patterson function and one cannot discern its structure in Fig. 5. A plot (not shown) of the A_{model} - and D_{model} -Patterson maps for a non-centrosymmetric fully ordered model of TiGePt is essentially identical to Fig. 5, confirming the main details of the structural model.

Fig. 6 shows the D_{obs} - and D_{model} -Patterson map of TiGePt along the line $[u \ u \ u]$ for the Mo data set. The model is that of the non-centrosymmetric and fully ordered structure. There is just one peak in the D_{obs} -plot at u = 0.25, corresponding to the Ge \rightarrow Pt and Pt \rightarrow Ti interatomic vectors. There is no peak at $[0 \ 0 \ 0]$ as the interatomic vectors at this point are self-vectors of zero height in a *D*-Patterson function. Likewise there is no peak at $[\frac{1}{2} \frac{1}{2}]$ as this point contains contributions from the Ti \rightarrow Ge and Ge \rightarrow Ti vectors which annihilate one another. The rest of the D_{obs} -Patterson map is a noisy background rising to its largest value of |P| of 137 066, about 20% of the peak value 620 750 at u = 0.25. The D_{model} -Patterson map has a peak at the same place as the D_{obs} -Patterson map (at u = 0.25) and with the same height within experimental uncertainty. There is thus excellent agreement between the observed and model Patterson functions for the Mo data set. Unsurprisingly, the background of the D_{model} -Patterson map is less noisy than that



Figure 6

 D_{obs}^{-} and D_{model}^{-} Patterson maps of TiGePt along the line $[u \, u \, u]$. Mo data set.



Figure 7

 $D_{\rm obs}\text{-}$ and $D_{\rm model}\text{-} {\rm Patterson}$ maps of TiGePt along the line $[u\,u\,u].$ Ag data set.

of the D_{obs} -Patterson. The observation of the peak at u = 0.25in the D_{obs} -Patterson map is most significant. This peak would occur neither with a centrosymmetric structure nor with a noncentrosymmetric crystal twinned by inversion in a ratio close to 50:50. The D_{obs} -Patterson map proves beyond doubt that the crystal structure is non-centrosymmetric, space group $F\bar{4}3m$, and the crystal measured is not twinned by inversion. The non-centrosymmetric fully ordered model reproduces this peak entirely satisfactorily.

For the Patterson maps calculated from the Ag data set, the $D_{\rm obs}$ and $A_{\rm obs}$ plots (not shown) correspond very closely to those presented in Fig. 5. Likewise the $D_{\rm model}$ and $A_{\rm model}$ plots (not shown) correspond very closely to those from the Mo data set. However, the $D_{\rm obs}$ -Patterson map for the Ag data set shown in Fig. 7 is far more noisy than that in Fig. 6 for the Mo data. This is often observed in residual density maps and is most probably caused by the larger range of $\sin \theta/\lambda$. Also reference to Table 1 shows a large difference in f'' of Pt for the two radiations. One could not conclude from Fig. 7 that the structure is definitely non-centrosymmetric.

8. Concluding remarks

For the intermetallic compound TiGePt with a non-centrosymmetric space group but atoms in positions of high point symmetry, statistics that are based only on observed values of D give the most reliable results in indicating whether the crystal structure is non-centrosymmetric or not. In particular, we note that the R_{merge} on A_{obs} and D_{obs} of complete sets of $m\bar{3}m$ general reflections and the D-Patterson maps work very well with the Mo data. These unequivocally indicate that the structure is non-centrosymmetric.

The ordered picture of the structure of TiGePt (*i.e.* the noncentrosymmetric one) is further supported by coherentpotential approximation (CPA) calculations of the band structure, which reveal a significantly higher energy of 1.2 eV per formula unit for the disordered structure in the space group $Fm\bar{3}m$ (Ackerbauer *et al.*, 2012).

The results presented in the current paper confirm the contention of Flack *et al.* (2011) that the A- and D-Patterson maps are useful techniques to employ in the validation of a crystal-structure determination. In general, peaks and troughs occurring at identical positions in an $A_{\rm obs} - A_{\rm model}$ and a $D_{\rm obs} - D_{\rm model}$ Patterson map of a crystal-structure determination are strong indications of some weakness in the structural model. The major current handicap to the use of these Patterson functions is the lack of software.

From the evidence presented in this paper, one discerns a distinct difference in the potentialities of the data set measured at 100 K with Mo $K\alpha$ radiation from that at 295 K with Ag $K\alpha$ radiation. Ag $K\alpha$ is a natural choice for a heavy element compound with a small unit cell if the atomic parameters, both positional and displacement, are of prime interest. However, this data, due to the lower resonant scattering especially for Pt (see Table 1), does not lead to a viable study of the absolute structure. With Mo $K\alpha$ radiation one can make good use of the intensity differences between Friedel

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opposites, even though there are fewer data for determining the atomic parameters. Thus, with the data available to this study, one sees that some techniques make a clearer distinction than others between two models. Moreover, the present work also suggests that for a problem as difficult as deciding whether TiGePt is centrosymmetric or not, a more conclusive answer requires up to three experiments at the absorption edges of Pt, Ti and Ge rather than higher resolution data at a single wavelength. Such additional experiments are beyond the scope of the current paper.

APPENDIX A

Expressions for A_{model} and D_{model} for stoichiometric TiGePt with fully occupied sites

$$H = h + k + l \tag{1}$$

$$f = f^{o} + f' \tag{2}$$

$$\phi_{\rm GT} = (2p - 1)(f_{\rm Ge} - f_{\rm Ti})$$
 (3)

$$\phi_{\rm GT}'' = (2p - 1) \left(f_{\rm Ge}'' - f_{\rm Ti}'' \right) \tag{4}$$

$$A(H = 4n) = \left[f_{\rm Pt} + f_{\rm Ge} + f_{\rm Ti}\right]^2 + \left[f_{\rm Pt}'' + f_{\rm Ge}'' + f_{\rm Ti}''\right]^2 \quad (5)$$

$$D(H=4n) = 0 \tag{6}$$

$$A(H = 4n + 2) = \left[f_{\rm Pt} - f_{\rm Ge} - f_{\rm Ti}\right]^2 + \left[f_{\rm Pt}'' - f_{\rm Ge}'' - f_{\rm Ti}''\right]^2$$
(7)

$$D(H = 4n + 2) = 0 \tag{8}$$

$$A(H = 4n + 1) = f_{Pt}^2 + \phi_{GT}^2 + f_{Pt}^{"2} + \phi_{GT}^{"2}$$
(9)

$$D(H = 4n + 1) = 4f_{\rm Pt}\phi_{\rm GT}'' - 4\phi_{\rm GT}f_{\rm Pt}''$$
(10)

$$A(H = 4n - 1) = f_{\rm Pt}^2 + \phi_{\rm GT}^2 + f_{\rm Pt}^{"2} + \phi_{\rm GT}^{"2} \qquad (11)$$

$$D(H = 4n - 1) = -4f_{\rm Pt}\phi_{\rm GT}'' + 4\phi_{\rm GT}f_{\rm Pt}''$$
(12)

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