J|A|C|S
COMMUNICATIONS

Published on Web 02/24/2007

$GdCo_{1-x}Ga_3Ge$: Charge Density Wave in a Ga Square Net

Marina A. Zhuravleva,[†] Michel Evain,[‡] Vaclav Petricek,[§] and Mercouri G. Kanatzidis*,[⊥]

Department of Chemistry, Michigan State University, East Lansing, Michigan 48823, I.M.N., UMR CNRS C6502, Institut des Materiaux Jean Rouxel, Laboratoire de Chimie des Solides, 2 rue de la Houssiniere, BP 32229, 44322 Nantes Cedex 03, France, Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 180 40 Praha 8, Czech Republic, and Department of Chemistry, Northwestern University, Evanston, Illinois 60208

Received December 21, 2006; E-mail: mkanatzidis@northwestern.edu

Charge density waves (CDWs) are nonuniform distributions of electronic charge that form in the Fermi sea of metals. Along with superconductivity and spin-density waves, they are one of the fundamental broken symmetry ground states, and one or other of these competing states appears at low temperature in nearly all metals.[1] The striped and checkerboard patterns of charge recently observed in high-temperature superconductors,[2] being possibly fundamental in understanding their properties, are a form of CDW. Symmetry, dimensionality, and disorder are intimately connected with CDWs and play a decisive role in critical phenomena.[3] Therefore, understanding the underlying bonding within the CDW itself is of fundamental interest.[1−4] Solving the quantitative structure of CDW materials, however, is difficult due to their small amplitude that results in very weak superlattice Bragg peaks that are not easy to quantify using X-rays. Apart from a few notable successes,[1] these patterns of atomic displacements have not been widely determined.

The square lattices formed by the late main group elements, such as pnicogens or chalcogens, are good candidates for CDW phenomena. Tellurium square lattices, for instance, are almost always subject to CDW distortions[5] giving rise to polytelluride oligomers and anomalous electronic transport phenomena.[6] Square sheets made of trielides (group 13) and tetrelides (group 14), on the other hand, are generally regarded to be stable atomic arrangements. Thus, normally intermetallics are not known to exhibit CDW phenomena. However, new findings indicate that the germanium square lattices could also be susceptible to distortions. For instance, the crystal structure of Tb_4FeGe_8[7] shows that the distortions so typical for chalcogenides may as well occur in other square nets.

When studying complex intermetallics of the RE/M/Ga/Ge system, we find plentiful examples of square nets. For $RE_3Ni_3Ga_8Ge_3$ and $RECoGa_3Ge$ (RE = Sm, Gd)[8] conventional X-ray diffraction methods suggest the presence of ideal Ga-square nets. Electron diffraction experiments, however, show evidence for long-range modulations which vary from compound to compound. For $GdCoGa_3Ge$, careful X-ray diffraction experiments indicated that the reciprocal lattice exhibited incommensurately spaced supercell reflections. On the basis of these, we successfully solved the modulated structure using a superspace crystallographic approach. Here we report the first example of a CDW in a square net of group 13 atoms and its structural details. $GdCoGa_3Ge$ exhibits a CDW in the Ga square net with an unexpected pattern of short and long Ga−Ga distance fluctuation.

For data collection, several crystals of $GdCo_{1-x}Ga_3Ge$ were tested for quality.[9] Analyses of the frames revealed two sets of spots corresponding to (a) strong intensity Bragg vectors that could be indexed with a tetragonal cell and (b) additional vectors of much weaker intensity at positions incommensurate with the tetragonal lattice. The lattice parameters were least-squares refined[10] from the positions of 980 reflections and a $(3+1)D$ indexing: $a_s = 4.1648(8)$ Å, $c_s = 23.774(14)$ Å, $\mathbf{q} = 0.3043(12)\mathbf{a}^*$. The intensity integration and analytical absorption corrections were carried out with the Jana2000 program.[11] At first, it appeared that the crystal exhibited modulation along both the *a*- and *b*-directions, but the true aperiodic structure actually was not of tetragonal symmetry but orthorhombic, exhibiting rotational pseudomerohedral twinning.[12] Taking into account twinning, the original set of 91236 reflections was merged according to the $(mmm, \bar{1}11)$ $(3+1)D$ point group, yielding an internal R value of 0.0678 [$I \geq 2\sigma(I)$]). The application of twin law could not unravel the disordered nature of the structure. The observed disorder was thus assigned to an incommensurate aperiodic ordering of the disordered atoms leading to what appears to be a CDW.

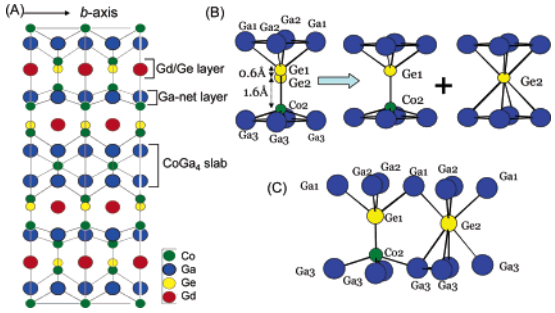

Figure 1. (A) Average structure of $GdCoGa_3Ge$. (B) Average coordination around disordered Co2 and Ge1/Ge2 atoms in the 3D basic structure (left); ordering model for the disordered fragment (right). (C) Ordered environment of the Co2, Ge1, and Ge2 atoms in a fragment of the modulated structure. Note that averaging over these two would produce a disordered picture given in Figure 1B.

Figure 1 depicts the disordered orthorhombic substructure of $GdCo_{1-x}Ga_3Ge$ (obtained by ignoring the weak reflections due to the modulation) and an excised fragment thereof where the Ge1, Ge2, and Co2 atoms are partially occupied (50% each) and located at nonphysical distances to each other. Three building blocks are marked out: a Gd/Ge layer, a Ga-net layer and the [$CoGa_4$] slab. This average disordered picture simply indicates that when Ge2 is present, Ge1 and Co2 are absent, and vice versa. As the observed incommensurate modulation originated from an aperiodic ordering of the Co2 and Ge1/Ge2 atoms and the distortion in the Ga-net, the complete structure solution required the application of superspace formalism.[13] From the systematic absences, $Immm(\alpha 00)00s$ was identified as the probable superspace group.[14] A classical model with harmonic functions was employed to model the occupations of Co2 and Ge1/Ge2 atoms.

[†] Michigan State University.
[‡] I.M.N., UMR CNRS C6502, Institut des Materiaux Jean Rouxel.
[§] Institute of Physics, Academy of Sciences of the Czech Republic.
[⊥] Northwestern University.

10.1021/ja069195m CCC: $37.00

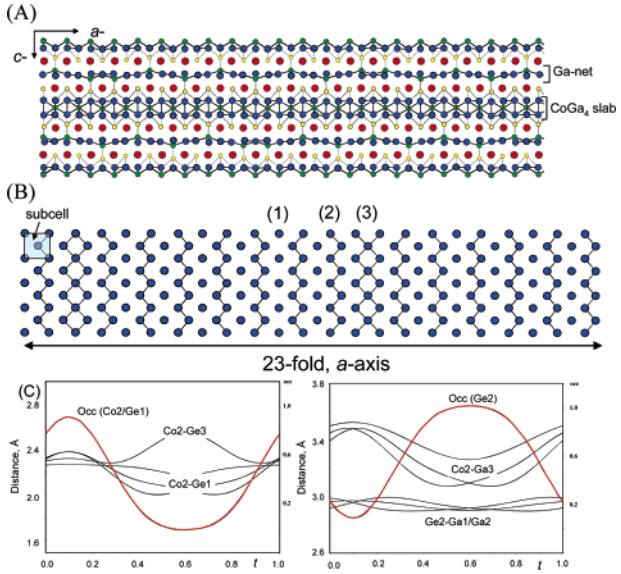

Figure 2. (A) Modulated, aperiodic structure of $GdCo_{0.86}Ga_3Ge$ viewed down the *b*-axis. (B) CDW pattern in the Ga-net viewed down the *c*-axis. The isolated Ga atoms, zig−zag single-atom chains and occasional ribbons indicated as (1), (2), and (3) respectively. A Ga3−Ga3 distance cutoff of 2.93 Å was used for the bond representation. (C) (left) Co2−Ge1 and Co2−Ga3 distances (solid line) and Co2 occupancy (red line) and (right) Ge2-Ga distances (solid line) and Ge2 occupancy (red line) as a function of the internal *t* coordinate.

A fragment of incommensurately modulated structure of $GdCo_{1-x}Ga_3Ge$ projected onto the *ac* plane is shown in Figure 2A. The structure is a simple ordered model for Co2(Ge1) and Ge(2) atoms, Figure 1C. Complete information on data collection and refinement are provided in the Supporting Information Section.

A detailed consideration of the modulated structure reveals that the layer which contains the Ga-square net shows its distortion into sequences of isolated Ga atoms and infinite one-dimensional polygallide entities, see Figure 2B. The distortion takes on the most severe, bond-breaking character along the *a*-axis direction which is an approximately 23-fold superstructure. While in the average substructure (Figure 2B, subcell) the Ga−Ga interactions are of weakly bonding to nonbonding character (2.94 Å), in the superstructure the bonding and the nonbonding interactions are clearly distinctive. Namely, the CDW comprises a sequence of isolated Ga atoms, zig−zag single-atom chains, and occasional ribbons indicated as (1), (2), and (3) respectively in Figure 2B. The Ga−Ga bonds within the chains are as short as 2.61 Å whereas outside the chains range from 2.94 to well over 3 Å. This short−long distance alternation pattern represents a bona fide CDW reminiscent of those found in the electron-rich Te square network of $NdTe_3$.[15]

The Gd/Ge layers adjust to the perturbation brought about by the CDW in the Ga-net layer by shifting the Ge atoms toward or away from the Gd plane. The occupancy modulation along with the distances involving Co2(Ge1) and Ge2 atoms of the disordered fragment are shown in Figure 2C. The most drastic variation of the atomic shift with the internal coordinate *t* is observed for the Ge2 atom. The maximal and minimal Ge2−Ga3 distance, for example, varies by nearly 0.3 Å at different values of *t*. The Co2 shift with respect to Ga3 is also substantial, on the order of ∼0.2 Å. The Co2−Ge1 bond distance range is less dispersed (∼0.1 Å), and Ge2−Ga1 varies even less than that with *t*. The nonstoichiometry in the compound comes from the partial occupancy of Co2 atoms, resulting in the formula $GdCo_{0.86}Ga_3Ge$.

We seem to have discovered a new type of CDW in the intermetallic compound $GdCoGa_3Ge$. To our best knowledge this is the first example of a CDW on a Ga square net. Moreover, the structural features revealed are unique among known CDW nets. Such detailed information is critical to a complete understanding of CDWs in a wide variety of chemical systems, as it is a prerequisite to enabling and validating ab initio electronic structure calculations on such systems. Although it is not yet clear what causes the CDW in this case, electronic reasons are a plausible explanation.[1−3] In CDW systems generally the **q**-vector is shown to correspond to nesting features of a simplified model of the Fermi surface. The distortion from the ideal structure leads to the so-called CDW gap which can be probed with angle-resolved photoemission spectroscopy and indirectly with charge-transport measurements.[16,6] Whether this is also the case for $GdCoGa_3Ge$ remains to be seen.

Acknowledgment. Financial support from the Department of Energy (DE-FG02-99ER45793) is gratefully acknowledged. We thank S. J. L. Billinge and S. D. Mahanti for fruitful discussions.

Supporting Information Available: Experimental details of data collection and refinement, tables of crystallographic data, and related information for $GdCo_{0.86}Ga_3Ge$. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Gruener, G. *Density Waves in Solids*; Addison-Wesley: New York, 1994. (b) Vershinin, M.; Misra, S.; Ono, S.; Abe, Y.; Ando, Y.; Yazdani, A. *Science* **2004**, *303*, 1995. (c) Hoffman, J. E.; Hudson, E. W.; Lang, K. M.; Madhavan, V.; Eisaki, H.; Uchida, S.; Davis, J. C. *Science* **2002**, *295*, 466.

(2) Hanaguri, T.; Lupien, C.; Kohsaka, Y.; Lee, D. H.; Azuma, M.; Takano, M.; Takagi, H.; Davis, J. C. *Nature* **2004**, *430*, 1001.

(3) Loudon, J. C.; Cox, S.; Williams, A. J.; Attfield, J. P.; Littlewood, P. B.; Midgley, P. A.; Mathur, N. D. *Phys. Rev. Lett.* **2005**, *94*, 097202.

(4) (a) Huang, F. Q.; Brazis, P.; Kannewurf, C. R.; Ibers, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 80. (b) Lee, S.; Foran, B. J. *J. Am. Chem. Soc.* **1996**, *118*, 9139.

(5) (a) Malliakas, C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2006**, *128*, 12612. (b) Patschke, R.; Kanatzidis, M. G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3266. (c) Kim, H.; Malliakas, C.; Tomic, A.; Tessmer, S.; Kanatzidis, M. G.; Billinge, S. *Phys. Rev. Lett.* **2006**, 96(22), Art. No. 226401.

(6) Ru, N.; Fisher, I. R. *Phys. Rev. B* **2006**, 73(3), Art. No. 033101.

(7) Zhuravleva, M. A.; Bilc, D.; Pcionek, R. J.; Mahanti, S. D.; Kanatzidis, M. G. *Inorg. Chem.* **2005**, *44*, 2177.

(8) Zhuravleva, M. A.; Pcionek, R. J.; Wang, X.; Shultz, A. J.; Kanatzidis, M. G. *Inorg. Chem.* **2003**, *42*, 6412.

(9) Data collection was carried out at room temperature on the KappaCCD diffractometer, using two different exposure times to overcome overflow scans and a high $\sin(\theta)/\lambda = 0.87$ cutoff ($\theta_{max} = 38°$). Radiation: Mo K-$L_{2,3}$ ($\lambda = 0.71073$ Å).

(10) Evain, M. *U-Fit*, a cell parameter refinement program; Institut des Matériaux Jean Rouxel: Nantes, 1992.

(11) Petricek, V.; Dusek, M. *JANA2000*, a crystallographic computing system; Academy of Sciences of the Czech Republic: Prague, 2000.

(12) This was suggested by the often-observed splitting of main spots for $GdCo_{1-x}Ga_3Ge$. The simplest possible twinning was the exchange of the *a* and *b* axes of an orthorhombic lattice with two similar *a* and *b* cell constants (see Supporting Information for details).

(13) For a complete description of the concepts and notations used for incommensurate structures, see: (a) de Wolff, P. M. *Acta Crystallogr.* **1974**, *A30*, 777. (b) Janssen, T.; Janner, A.; Looijenga-Vos, A.; de Wolff, P. M. In *International Tables for Crystallography*; Wilson, A. J. C, Ed.; Kluwer Academic Publishers: Dordrecht, 1993; Vol. C, Chapter 9.8. (c) Van, Smaalen, S. *Cryst. Rev.* **1995**, *4*, 79.

(14) (a) Johnson, C. K.; Levy, H. A. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Ed.; Kynoch Press: Birmingham, 1974; Vol. IV, p 311. (b) Kuhs, W. F. *Acta Crystallogr.* **1984**, *A40*, 133.

(15) Malliakas, C.; Billinge, S. J. L.; Kim, H. J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2005**, *127*, 6510.

(16) Brouet, V.; Yang, W. L.; Zhou, X. J.; Hussain, Z.; Ru, N.; Shin, K. Y.; Fisher, I. R.; Shen, Z. X. *Phys. Rev. Lett.* **2004**, 93(12), Art. No. 126405.

JA069195M