

A High-Temperature X-ray Study of the Displacive Phase Transition in MnCoGe

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The crystal structure of MnCoGe – with Ni₂In type at high temperature and ordered PbCl₂ (TiNiSi) type at low temperature – was refined with anisotropic thermal parameters from single-crystal counter data measured at temperatures above and below the diffusionless phase transition. Large changes in positional parameters result in differences in the coordinations of all atoms. Thermal parameters of Co are considerably larger in the high-temperature form. In the high-temperature structure thermal displacements are greatest in those directions along which atom motion occurs in producing the low-temperature form.

Introduction

Diffusionless, displacive phase transitions between the hexagonal NiAs type structure, and its derivative, distorted, orthorhombic version, the MnP type structure, are known for VS, CrAs, MnAs, CoAs, or closely related compositions (Wilson & Kasper, 1964; Franzen & Burger, 1968; Grønvold & Snildal, 1970; Boller & Kallel, 1971; Seltz & Kjekshus, 1973; and references therein). Similar transitions between the corresponding 'filled-up' versions, the hexagonal Ni₂In type structure and the orthorhombic PbCl₂-type structure, were observed for Ni₂Si (Toman, 1952; Frolov, Putintsev, Sidorenko, Gel'd & Krents, 1972) and more recently for MnCoGe and MnNiGe (Johnson, 1975). The present investigation was undertaken in order to gain a better understanding of the mechanism of these phase transitions. It is the first study in which thermal parameters were determined. Vibrational amplitudes in the high-temperature form are of interest with regard to the 'soft mode' model of displacive phase transitions.

Experimental

A sample with nominal composition Mn_{0.98}CoGe was kindly provided by V. Johnson of this laboratory. It had been prepared from the high purity elemental components by heat treatment (3 days at 1170 K) in evacuated, sealed, Al₂O₃-lined, silica tubes. Stoichiometric MnCoGe transforms between 398 and 458 K (Johnson, 1975). Composition Mn_{0.98}CoGe was found to transform at about 340 and 305 K on heating and cooling, respectively. The non-stoichiometric sample was preferred in the present investigation because the high-temperature structure could be investigated at relatively moderate temperatures at which the crystals do not react with their environment.

Small single crystals were obtained by repeated cycling of the polycrystalline sample through the transition temperature. The crystals were mounted on glass

fibers with high-temperature epoxy resin and kept at the desired temperatures by a stream of hot nitrogen as described earlier (Jeitschko, 1972). Buerger precession photographs, recorded above and below the transition temperature, showed the symmetries and space-group extinctions expected for the low-temperature PbCl₂ (*Pnma*) and high-temperature Ni₂In (*P6₃/mmc*) type structures.

Lattice constants for Mn_{0.98}CoGe at room temperature were obtained from Guinier-Hägg data, calibrated with high purity KCl ($a=6.2931 \text{ \AA}$), by least-squares refinement: $a=5.947$ (2), $b=3.826$ (1), $c=7.051$ (2) \AA , $V=160.42$ (5) \AA^3 . For the hexagonal high-temperature phase at the transition temperature, lattice constants were interpolated from data reported by Johnson (1975): $a=4.087$ (1), $c=5.316$ (3) \AA . To facilitate comparisons, the higher symmetry Ni₂In type structure will be represented in this account in terms of the lower symmetry PbCl₂ type structure. The lattice constants for the corresponding orthorhombic cell are $a_o=c_h=5.316$ (3), $b_o=a_h=4.087$ (1), $c_o=a_h/3=7.079$ (2) \AA , $V=153.8$ (1) \AA^3 . The temperature dependence of the lattice parameters is reported linear with an abrupt change at the phase transition. In view of the large differences between the low- and high-temperature cells, the temperature dependence of lattice parameters can be neglected in a comparison of the two structures.

In order to obtain accurate thermal parameters and to minimize absorption effects, a very small crystal was used for the structure refinements. It approximated the shape of a sphere with a radius of about 0.016 mm. The crystal was mounted with random orientation (to minimize double diffraction) in an automated four-circle goniometer. Zr-filtered Mo radiation was used with scintillation counter and pulse-height discriminator. Scan angles were 2° along 2θ plus the angular separation of the $K\alpha$ doublet. Scan speed was 0.8° min^{-1} and background was counted for 20 s at both ends of the scans. For the low-temperature structure all reflections within 95° 2θ were measured at room temperature for five reciprocal lattice octants (a total of 3180 reflec-

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tions). For the high-temperature hexagonal structure, data were collected at 343 K up to $85^\circ 2\theta$ for one octant (285 reflections) of the corresponding low-temperature orthorhombic cell (which contains three equivalent data sets of the hexagonal cell).

Structure refinements

In the high-temperature ordered Ni₂In type structure, atomic positions are fixed by symmetry and only thermal parameters were refined. For the refinement of the low-temperature ordered PbCl₂ type structure, starting parameters were taken from TiNiSi (Shoemaker & Shoemaker, 1965). A full-matrix least-squares program by Finger (1969) was used. Atomic scattering factors were taken from Cromer & Mann (1968), corrected for anomalous dispersion (Cromer & Liberman, 1970). The function $\sum w(KF_o - |F_c|)^2$ was minimized, where w is the weight based on counting statistics and K a scale factor. Reflections for which F was less than one standard deviation were given zero weight.* A correction for secondary extinction was considered unnecessary. The repeated cycling through the transition temperature mentioned above resulted not only in a breaking up of large crystals, but obviously also in an increase in their mosaic character. Occupancy parameters for the metal positions were refined from the room-temperature data and held at those values in the final refinement of the high-temperature data. In previous refinements of the high-temperature data with simultaneous variation of occupational and thermal parameters, occupancy parameters were practically the same (0.996 ± 0.015 for Mn and 0.970 ± 0.016 for Co) as in the refinement of the low-temperature data.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30830 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Final parameters and conventional R values are summarized in Table 1. These values resulted from data obtained by averaging all equivalent reflections. Failure to account fully for absorption (caused by deviations from spherical crystal shape) affects the reliability of the thermal parameters. In order to evaluate this effect, the three equivalent data sets of one reciprocal lattice quadrant, collected at 343 K, were also refined separately. The results of these refinements are shown in Table 2. It can be seen that for all atoms, the long and short axes of the thermal ellipsoids correspond in the three refinements, and it is concluded that the refinements with the averaged data sets should also give a good quantitative representation of r.m.s. displacements.

The small size of the data crystal resulted in poor counting statistics for many weak reflections. Thus the overall R values are rather high. In refinements where

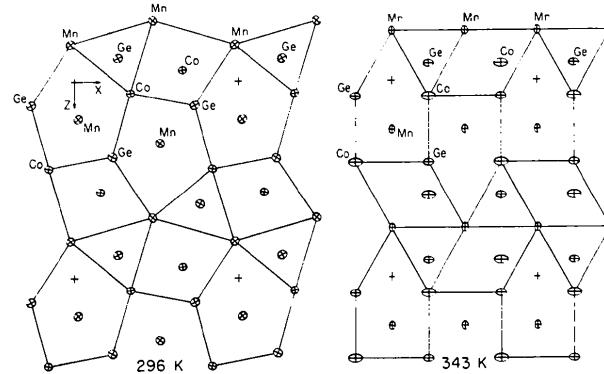


Fig. 1. Crystal structure of Mn_{0.98}CoGe below and above the transition temperature. The unit cell corresponding to the low-temperature ordered PbCl₂ (TiNiSi) type structure is indicated by crosses. Atoms at $z = \frac{1}{2}$ are connected by lines, atoms at $z = \frac{1}{4}$ are unconnected. Thermal ellipsoids are plotted at the 50% probability limit.

Table 1. Results of least-squares refinements of Mn_{0.98}CoGe

Vibrational parameters ($\times 10^4$) are defined through $T = \exp(-\sum h_i h_j \beta_{ij})$. Numbers in parentheses are e.s.d.'s in the least significant digits. The last two lines contain the conventional R values (number of unique reflections given in parentheses), of which the first one excludes reflections with $F_o > \sigma$, which were assigned zero weight in the least-squares refinements. All results are given in terms of the low-temperature space group $Pnma$.

Temperature (K)	296			343		
	TiNiSi			Ni ₂ In		
Structure type	Mn	Co	Ge	Mn	Co	Ge
Scattering factor						
Occupancy	0.997 (7)	0.974 (6)	1*	0.997*	0.974*	1*
x	0.0234 (2)	0.1581 (2)	0.7660 (1)	0	$\frac{1}{4}$	$\frac{3}{4}$
y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
z	0.1899 (1)	0.5593 (1)	0.6198 (1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
β_{11}	52 (2)	51 (2)	62 (2)	34 (6)	186 (9)	103 (6)
β_{22}	87 (5)	60 (4)	62 (3)	102 (7)	95 (8)	66 (6)
β_{33}	35 (2)	26 (1)	37 (1)	$\beta_{22}/3$	$\beta_{22}/3$	$\beta_{22}/3$
β_{12}	0	0	0	0	0	0
β_{13}	-6 (1)	2 (1)	6 (1)	0	0	0
β_{23}	0	0	0	0	0	0
Equivalent B (\AA^2)	0.64 (2)	0.53 (2)	0.66 (2)	0.58 (4)	1.12 (6)	0.69 (4)
$R (F_o > \sigma)$		0.051 (572)			0.064 (104)	
R (all reflections)		0.060 (636)			0.076 (118)	

* Held constant

data with $F_o < 3\sigma$ were excluded, the R values were smaller by about 0.015; none of the positional or thermal parameters differed by more than 30% of their standard deviations, which were about 15% higher than those obtained in the previous refinements.

Results and discussion

Although the overall composition of the sample $Mn_{0.98}CoGe$ is slightly deficient in Mn, the occupancy refinements show that the defects actually occur for the Co positions. This is not surprising since many phases are known with defect-Ni₂In (*e.g.* NiAs type structures (Pearson, 1967) where the defects occur for those positions which correspond to the Co site in MnCoGe. Thus the crystal chemical composition of the compound investigated in the present study is probably better described by the formula $(Mn_{0.98}Co_{0.02})Co_{0.98}Ge$.

The high- and low-temperature structures of MnCoGe are compared in Fig. 1. Near neighbor distances and coordination numbers (CN) are shown in Fig. 2 and Table 3. In both forms all atoms have high CN, as is typical for intermetallic phases. When compared with the sum of the CN 12 radii, however, the metal–metal distances are greater and the metal–metalloid distances are shorter in general, as was noted before for compounds with similar compositions (Jeitschko, 1969, 1970). Thus it can be assumed that the bonding metal–germanium states have a higher population than the metal–metal bonding states.

During the phase transition all atoms show changes

in their coordination. The high-temperature phase is stabilized by one additional Mn–Ge, one Co–Ge, and two Mn–Mn bonds; the low-temperature form has two additional short Co–Co interactions per formula unit.

These differences in bonding do not explain why one structure is stabilized over the other at different temperatures.* A comparison of thermal parameters shows that the Co atom has considerably larger vibrational amplitudes in the Ni₂In type form (compare B values of Table 1) and it can be concluded that the higher entropy of the high-temperature form is due to the ‘rattling’ of the Co atom. Atomic displacements similar to those in MnCoGe, occur also in the phase transitions from the high-temperature hexagonal NiAs to the low-temperature orthorhombic MnP type structures where the Co positions of MnCoGe are empty. Thus lattice vibrations involving the Mn and Ge atoms in MnCoGe probably also contribute to the higher entropy of the Ni₂In (and NiAs) type phase.† It can be seen (Fig. 2, Table 2) that thermal displacements in

* It could be argued that the Ni₂In form of MnCoGe has on average higher CN which suggests an entropy increase due to greater delocalization of electrons. This argument is somewhat at variance with the bonding discussion given above. Certainly electronic entropy contributions alone are not responsible for the phase change.

† The phase transition in MnAs at about 313 K occurs in the opposite direction from a low-temperature NiAs type to a high-temperature MnP type structure (Wilson & Kasper, 1964; Seltze, Kjekshus & Andresen, 1974). There obviously the entropy changes due to disorder of magnetic spins outweigh the lattice dynamical entropy differences.

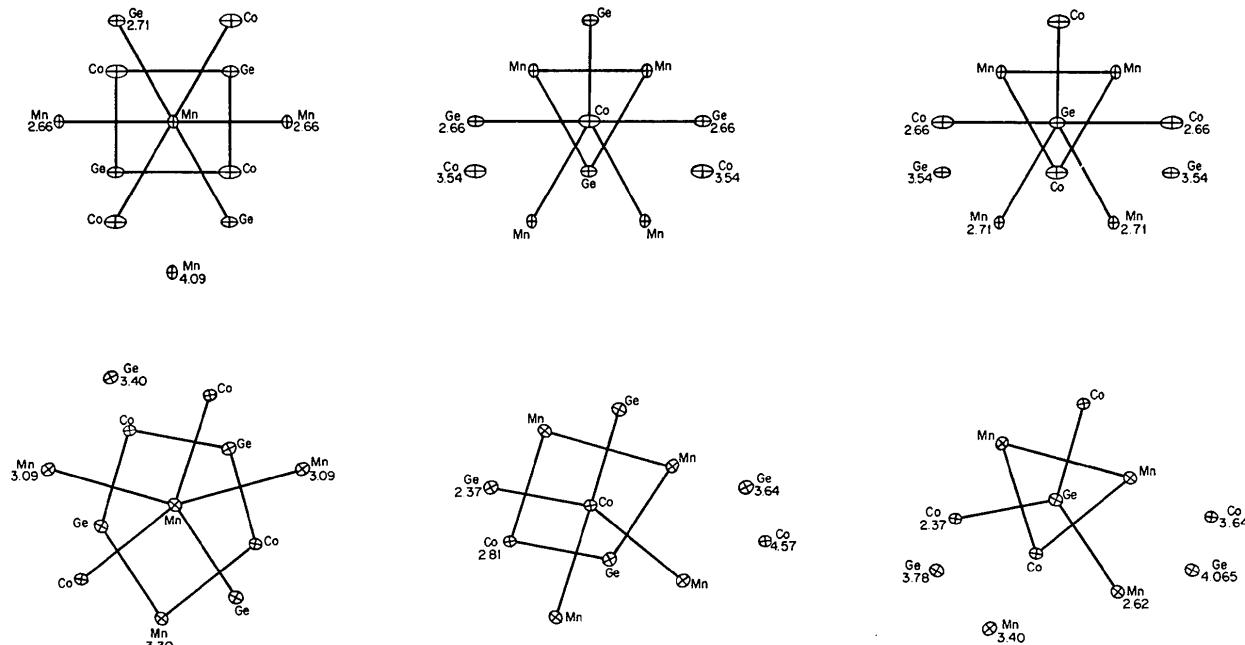


Fig. 2. Near-neighbor coordinations in $Mn_{0.98}CoGe$ in the high-temperature Ni₂In type form (upper half) and in the low-temperature PbCl₂ type form (lower half of the figure). Atoms connected by lines to the central atom are at the same height as the central atom. Atoms connected to each other but not to the central atom are $\frac{1}{2}$ translation period above and below the central atom. Distances toward the central atom are indicated in Å.

Table 2. Root-mean-square amplitudes (\AA) of thermal displacements in the Ni_2In form of $\text{Mn}_{0.98}\text{CoGe}$ at 343 K

The last three columns contain the results for least-squares refinements with the three different equivalent data sets before averaging, in order to demonstrate the influence of absorption effects. Standard deviations are given in parentheses.

	Direction*	Averaged data	I	II	III
Mn	<i>a</i>	0.069 (6)	0.067 (7)	0.077 (7)	0.066 (10)
	<i>b, c</i>	0.093 (3)	0.101 (4)	0.088 (4)	0.089 (5)
Co	<i>a</i>	0.163 (4)	0.167 (6)	0.173 (11)	0.154 (8)
	<i>b, c</i>	0.090 (4)	0.092 (5)	0.085 (12)	0.091 (5)
Ge	<i>a</i>	0.121 (3)	0.124 (5)	0.125 (8)	0.113 (7)
	<i>b, c</i>	0.076 (3)	0.080 (4)	0.074 (6)	0.076 (6)

* Crystal axis to which the axis of the thermal ellipsoid is parallel.

Table 3. Interatomic distances in $\text{Mn}_{0.98}\text{CoGe}$

The distances for the low-temperature (TiNiSi type) and the high-temperature (Ni_2In type) structures are compared one by one and their differences are listed. All distances shorter than 3.3 \AA are given. Standard deviations are all 0.001 \AA or less. Major changes in coordination numbers (CN) and interatomic distances are printed boldface.

	TiNiSi type	Ni_2In type	Δ
Mn: 1 Ge	2.617	2.708	-0.091
2 Ge	2.620	2.708	-0.088
2 Ge	2.650	2.708	-0.058
1 Ge	3.396	2.708	+0.688
1 Co	2.725	2.708	+0.017
1 Co	2.794	2.708	+0.086
2 Co	2.820	2.708	+0.112
2 Co	2.845	2.708	+0.137
2 Mn	3.092	2.658	+0.434
CN:	11	14	+3
Co: 2 Ge	2.336	2.360	-0.024
1 Ge	2.352	2.360	-0.008
1 Ge	2.370	2.658	-0.288
1 Ge	3.640	2.658	+0.982
1 Mn	2.725	2.708	+0.017
1 Mn	2.794	2.708	+0.086
2 Mn	2.820	2.708	+0.112
2 Mn	2.845	2.708	+0.137
2 Co	2.810	3.539	-0.729
CN:	12	11	-1
Ge: 1 Mn	2.617	2.708	-0.091
2 Mn	2.620	2.708	-0.088
2 Mn	2.651	2.708	-0.057
1 Mn	3.396	2.708	+0.688
2 Co	2.336	2.360	-0.024
1 Co	2.352	2.360	-0.008
1 Co	2.370	2.658	-0.288
1 Co	3.640	2.658	+0.982
CN:	9	11	+2

the high-temperature form are greatest in those directions along which atom motion occurs in producing the low-temperature form. This is to be expected from the 'soft mode' model of diffusionless phase transitions (Cochran, 1969), since ideally, frequency and amplitudes of thermal motion are inversely proportional, and therefore soft lattice modes correspond to large atomic displacements. Since, however, the thermal displacements are not exceptionally large, the lattice is

also not very 'soft' at this temperature ($\sim 38 \text{ K}$ or $\sim 3 \text{ K}$ above the transition temperature on cooling or heating, respectively).

The phase transition in MnCoGe is diffusionless and involves a change in crystal system. It can therefore be classified as ferroelastic (Aizu, 1970; Jeitschko & Sleight, 1974).

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