Crystal Structure and Magnetic Susceptibility of a Ru_2Si_3 Single Crystal

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Abstract

X-ray diffraction photographic experiments and anisotropic magnetic susceptibility measurement were made to examine the crystal structure of a Ru_2Si_3 single crystal. The X-ray analysis revealed that the single crystal possesses a tetragonal symmetry. Some very weak X-ray diffraction spots suggest a superstructure with 4-times larger lattice constants than those of the conventional tetragonal lattice. It was found from the susceptibility measurement that the single crystal is diamagnetic at low temperatures ranging from 20K to 300K, and that the susceptibilities are uni-axially anitotropic, which is consistent with the results of the X-ray diffraction experiments. It is concluded from the diamagnetic susceptibilities that coordinate bonding is established between Si and Ru atoms, which is consistent with the results of a previous magnetic susceptibility analysis of $CrSi_2$.

Introduction

Ru_2Si_3 is known as a thermoelectric semiconductor useful at high temperatures [1], [2]. Although many investigations [3]-[9] have been made on this compound, detailed crystal structure have not been clarified yet. Two different types of crystal structures are known: viz., a tetragonal structure [3] and orthorhombic structures with a variety of lattice constants [5],[6],[8] as shown in Table 1. A report suggests a transform from a low-temperature orthorhombic centrosymmetric structure to a high-temperature tetragonal non-centrosymmetric structure [9].

crystal system	lattice constants	ref.
tetragonal	a=1.1075nm, c=0.8954nm*1 (single crystal sample)	[3]
orthorhombic	a=1.1060nm, b=0.8952nm, c=0.5530nm*2 (twined crystal sample)	[5]
	a=1.1057nm, b=0.8934nm, c=0.5533nm (arc-melted sample)	[6]
	a=1.10678nm,b=0.8975nm,c=0.55339nm (arc-melted sample)	[8]

*1: JCPDS#18-1141
*2: JCPDS#32-978

Table 1 Lattice constants of Ru_2Si_3

It is known that Ru_2Si_3 possesses diamagnetic susceptibility [10]. It may be expected that the diamagnetism of Ru_2Si_3 reflects coordinate bonding between Ru and Si atoms in the same way as that of $CrSi_2$[11]. Detailed analysis, however, have not been made on the susceptibility yet.

In this work, X-ray diffraction photographic experiments were made to determine the crystal symmetry of a Ru_2Si_3 single crystal, and SQUID (Superconducting QUantum Interference Device) technique was utilized to examine the anisotropic magnetic susceptibilities of the crystal.

X-ray diffraction photographic experiments

Single crystal samples for X-ray and susceptibility experiments were cut out of the crystal grown by a Bridgman-like method [1]. Laue back reflection technique was utilized to determine the crystal axes. A Mo-target Coolidge tube was operated under the conditions of 20kV and 30mA for 8 hours. The distance between the crystal and the film was 30mm. It was found from the Laue photographs that the crystal has one 4-fold axis (c-axis) and two 2-fold axis (a_1- and a_2-axes). Figure 1 shows one of the Laue photographs taken in the direction of a 2-fold axis.

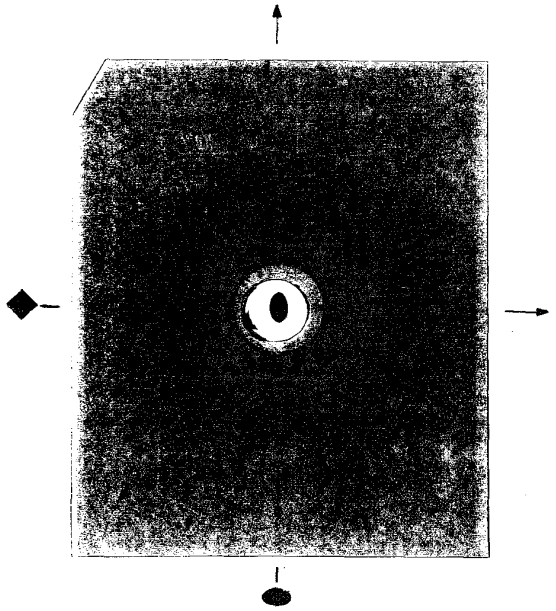
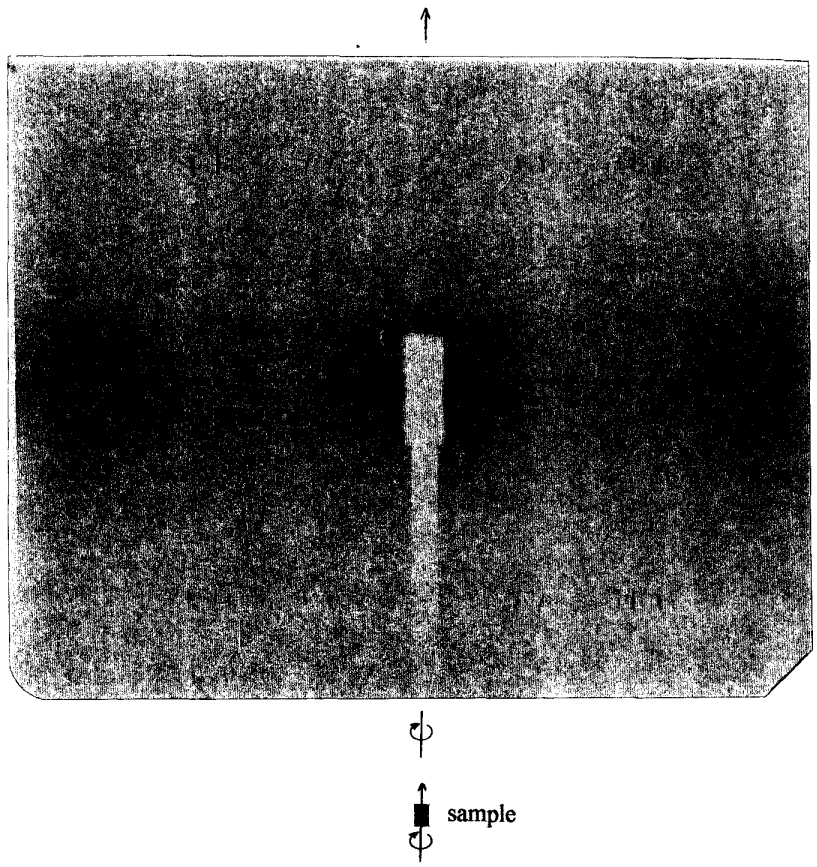


Fig. 1 Laue back reflection photograph of a Ru_2Si_3 single crystal .

The rotating crystal method was performed to determine the spatial period in the direction of a 2-fold axis. The crystal was rotated in the direction of the a_2-axis. A Cu-target Coolidge tube was operated under the conditions of 40kV and 30mA for 8 hours. The diameter of the camera was 57.4mm. Figure 2 shows one of the rotating crystal photographs. As shown in this figure, clear reciprocal lattice layers are recorded. The separations between the layers are consistent with the conventional tetragonal a-axis[3], viz., a_2=1.108nm. The diffraction spots of the odd-order layers are rather weak, which suggests a pair of similar sub-structures in the a_2 direction. It was also found from a detailed observation that a few very weak diffraction spots are not in agreement with the conventional tetragonal lattice. (It is, unfortunately, difficult to identify the very weak spots in this printed image.) The very weak diffraction spots suggest a superstructure with a 4-times larger crystal axis than that of the conventional tetragonal structure.



sample size: 0.2mm×0.2mm×0.4mm.

rotation axis: a_2-axis.

X-ray source: Cu-target 1.5kW Coolidge tube.

power: 40kV×30mA.

exposure time: 8 hours.

film: FUJI X-ray film #150.

Fig. 2 Rotating crystal photograph of a Ru_2Si_3 single crystal.

Weissenberg technique was performed to examine the a_1- and c-axes by means of the equi-inclination method. A Cu-target Coolidge tube was operated under the conditions of 40kV and 30mA for 8 hours. The diameter of the camera was 57.4mm. Most of diffraction spots observed were in good agreement with the conventional tetragonal lattice[3], viz., a_1=1.108nm and c=0.895nm. A few very weak diffraction spots, however, did not obey the conventional tetragonal diffraction rules. To observe the very weak diffraction spots in detail, the Weissenberg camera was operated for 20 hours. Figure 3 shows the Weissenberg photograph. Strong diffraction spots are in good agreement with the conventional tetragonal crystal structure. Some very weak diffraction spots do not obey the conventional diffraction rules. Figure 4 shows the diffraction spots (circles) and the reciprocal lattices of the conventional tetragonal structure (solid curves), to clarify the difference between the strong diffraction spots (open circles) in agreement with the conventional tetragonal structure and the very weak diffraction spots (closed circles) that does not obey the conventional diffraction rules. The very weak diffraction spots suggests a superstructure with a 4-times larger lattice constants (broken curves) than those of the conventional tetragonal structure.

The crystal was also rotated in the a_1-direction to take rotating crystal and Weissenberg photographs. It was confirmed from the photographs that the crystal possesses a tetragonal crystal symmetry.

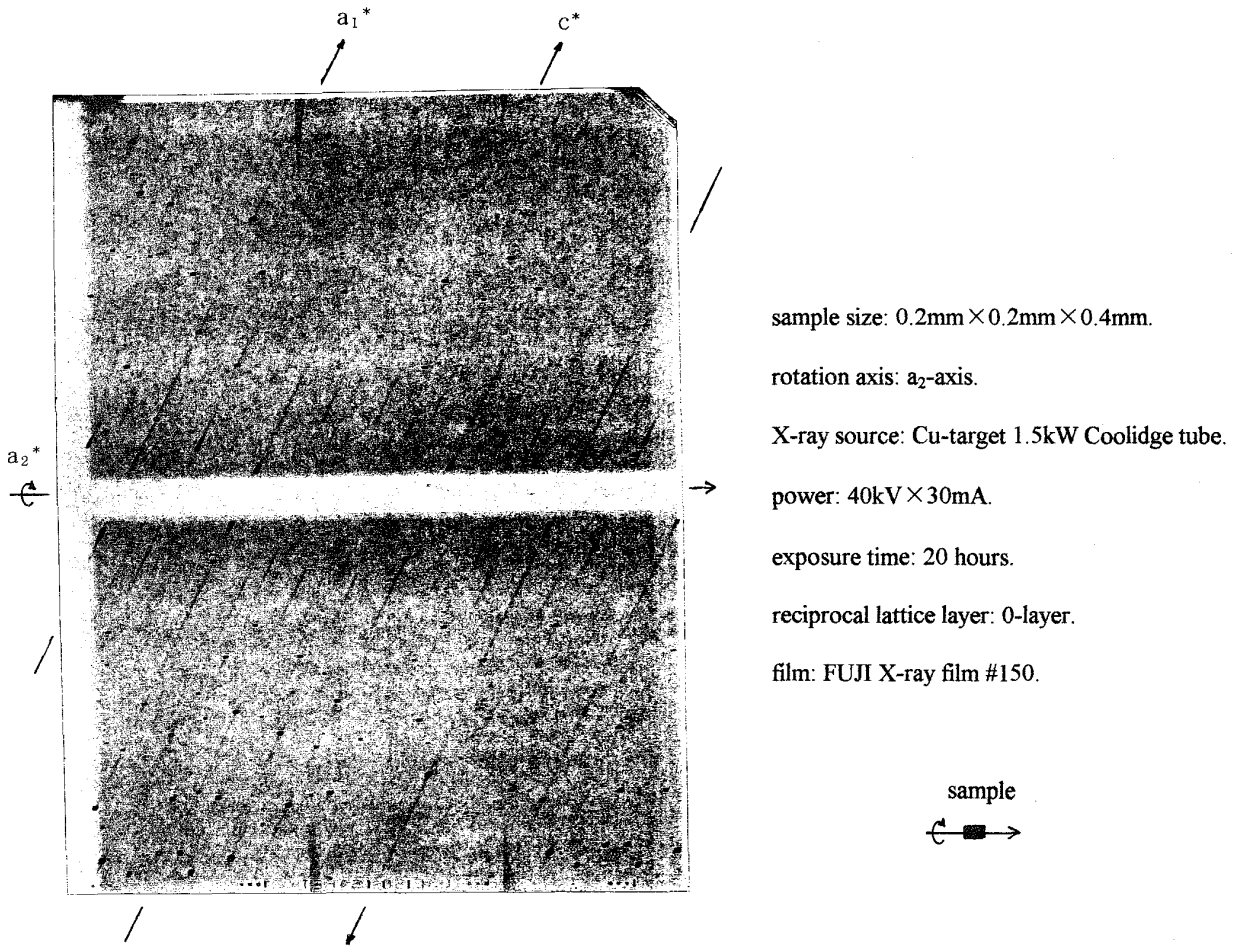


Fig. 3 Weissenberg photograph of a Ru_2Si_3 single crystal.

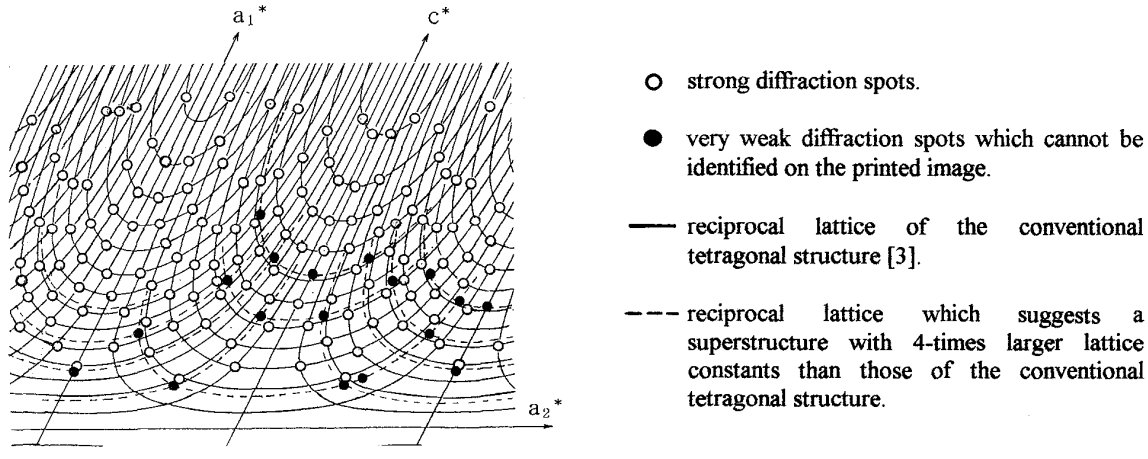


Fig. 4 Comparison of the X-ray diffraction spots with the reciprocal lattice.

Magnetic susceptibility measurement

Anisotropic magnetic susceptibilities of the Ru_2Si_3 single crystal were measured by utilizing SQUID technique at low temperatures ranging from 20K to 300K. A magnetic field of 0.1T was applied in the direction of a_1-, a_2- and c-axes. No hysteresis was observed within the applied field. Figure 5 shows the observed anisotropic susceptibilities. As shown in this figure, the diamagnetic susceptibilities in the c-direction are weaker than those in the other perpendicular directions over the whole temperature range observed. The difference between the susceptibilities in two 2-fold directions is negligible, which is consistent with the results of the X-ray photographic experiments mentioned above.

It is known that the anisotropic diamagnetic susceptibilities of $CrSi_2$ can be analyzed by means of the coordinate bonding between Cr and Si atoms [11]. It may be expected that the anisotropic susceptibilities of the Ru_2Si_3 single crystal reflect coordinate bonding between Ru and Si atoms in the same way as those of $CrSi_2$. The mean value of anisotropic susceptibilities shown in Fig.5 is estimated at about -190×10^{-6}emu/mol. It may be assumed that the chemical bonding in Ru_2Si_3 is mainly established by six *d* electrons of a Ru atom, while the remaining two outer electrons tends to localize at the Ru atom as a lone pair so that the inner core of the Ru forms a Kr-like core. Assuming the inner core of Si forms an Ar-like core, the contribution from the inner cores may be estimated at -130×10^{-6}emu/mol. It may be expected that in a Ru_2Si_3 lattice outer electrons localized as lone pairs at Ru atoms will enhance the diamagnetic contribution. It may be concluded form the uniaxial anisotropy in the c-direction that the lobes of the lone pair electrons localized at Ru atoms extend in the c-direction.

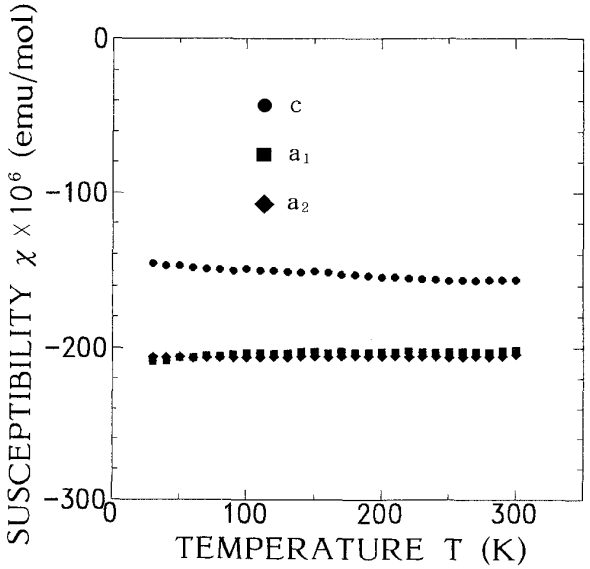


Fig. 5 Magnetic susceptibilities of a Ru_2Si_3 single crystal.

Conclusion

The results of the above discussions are concluded as follows:

(1) The present Ru_2Si_3 single crystal grown by a Bridgman-like method possesses a tetragonal crystal symmetry.

(2) Very weak X-ray diffraction spots suggest a superstructure with 4-times larger crystal axes than those of the conventional lattice.

(3) In a Ru_2Si_3 lattice, coordinate bonding is established between Ru and Si atoms in the same way as that in a $CrSi_2$ lattice.

(4) The anisotropy in magnetic susceptibilities suggests that the lobes of lone pair electrons localized at Ru atoms extend in the c-direction.

Acknowledgment

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