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Ru_3Sn_7 with the Ir_3Ge_7 structure-type

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Abstract

Millimeter-sized single crystals of the title compound have been grown from a Sn-rich melt and neutron diffraction data recorded at room temperature and 20 K have been used to confirm and refine the crystal structure. The Ir_3Ge_7 structure-type, cubic $Im\bar{3}m$ can be viewed as a framework of alternating corner linked Ru_6Sn_8 capped-octahedral clusters and Ru_2Sn_4 flattened-octahedral clusters, such that the latter form their own three-dimensional sublattice. The Ru–Sn distances determined for Ru_3Sn_7 fall in the middle of the observed range tabulated from the handful of known Ru–Sn distances in intermetallics. The resistivity of Ru_3Sn_7 is metallic, with a value of 72 $\mu\Omega$ cm at 300 K and 0.5 $\mu\Omega$ cm at 5 K. The magnetic susceptibility is diamagnetic at room temperature, but becomes paramagnetic as the temperature is lowered. We interpret the susceptibility as being due to a diamagnetic 'core' contribution and a paramagnetic contribution arising from the Ru d orbitals. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Ruthenium stannide; Intermetallic; Neutron diffraction

1. Introduction

The Ru_3Sn_7 phase has been encountered in searches for novel reentrant superconductors and magnetic materials in ternary stannides [1]. Although an entry has been long listed in the ICDD powder diffraction file, it apparently was overlooked for inclusion in the recent edition of the Pearson's Handbook of Crystallographic Data for Intermetallic Phases [2], and no crystal structure refinements have hitherto been reported.

2. Experimental

Single crystals of Ru_3Sn_7 were grown from a Sn-rich melt as follows. Ru powder (Johnson Matthey Puratronic, 99.99%) and Sn shot (Johnson Matthey, 99.999%) were combined in the ratio Ru:Sn=1:8 and sealed under vacuum in a silica ampoule. The ampoule was heated to 1150°C and then cooled to 425°C over the course of 30 h. Shiny, well-faceted crystals resulted. Excess flux was removed by etching in HCl.

Single crystal measurements employed the HB2a four-circle diffractometer, utilizing the 115 reflection from a Ge monochromator at a take-off angle of 45°. From this instrument configuration the neutron wavelength of 0.8378(2) Å was calibrated using a crystal of KCl ($a=6.2910$ Å). A euhedral crystal, $2\times2\times3$ mm^3 in size, was glued to an aluminum pin and mounted on the cold-tip of a closed-cycle He refrigerator, which is mounted on the diffractometer and used to control the temperature. For data collection at each temperature the same set of 60 reflections was used for refining the lattice parameter and determining the orientation matrix. The data collections were carried out by radially scanning through the Ewald sphere. At the limits of $2\Theta=0$ and 180° the radial scan is a pure ω scan and a pure Θ–2Θ scan, respectively; and in between a simple trigonometric relationship controls the relative speeds of the ω and 2Θ motors. A 1/8 sphere of Bragg reflections was measured to $\sin\Theta/\lambda=0.914$ $Å^{-1}$. Three intense reflections were monitored to correct the intensities for variations in the neutron flux, which did not vary by more than 1% for the duration of each data collection. The reflection intensities were integrated using the Lehmann–Larson algorithm and corrected for the Lorentz effect with the UCLA Crystallographic Software [3]. The linear neutron attenuation factor, including both incoherent scattering and absorption, for the crystal used in this study is small, 0.033 cm^{-1}. Psi-scans confirmed that absorption was not significant, so an absorption correction was not made. The scattering cross-sections used throughout were taken from [4]. The intensities of equivalent

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Table 1
Crystal structure data for Ru_3Sn_7, $Im\bar{3}m$, $Z=4$

Temperature	20 K	296 K
Cell a (Å)	9.3720(11)	9.3735(8)
ρ calc. (g cm^{-3})	9.150	9.146
Measured reflections	1628	1527
Merged reflections	299	299
Observed reflections	220	204
$R(F)$	0.0258	0.0269
$wR(F)$	0.024	0.022
Goodness of fit	1.646	1.839
U_{eq}(Sn1)	0.0016	0.0066
x(Ru)	0.34514(8)	0.34534(9)
U_{eq}(Ru)	0.0013	0.0049
x(Sn2)	0.16120(4)	0.16112(5)
U_{eq}(Sn2)	0.0021	0.0062

Atom positions: Sn1 12d 1/4,0,1/2; Ru 12e x,0,0; Sn2 16f x,x,x.

reflections were averaged in the cubic space group $Im\bar{3}m$. For the 296 K data collection 1527 reflections were measured, leading to 204 independent reflections with $F_{obs}/(\text{sigma } F)>1.5$. For a second data set at 20 K 1628 reflections were measured, leading to 220 independent reflections with $F_{obs}/(\text{sigma } F)>1.5$. For the two temperatures the data to parameter ratios are 18.5 and 20, respectively. Observed structure factors were used in least-squares refinement of the scale factor, atom positional parameters, and anisotropic temperature factors [5]. Extinction was significant and both a Becker–Coppens Type I and II corrections were refined. The large extinction correction is consistent with the crystal being brittle, hard, and having a narrow mosaic. In Table 1 the refinement results are summarized. Anisotropic atomic displacement parameters can be obtained from the authors upon request.

Resistivity measurements were performed using a linear four-probe method. Epo Tek H20 E silver epoxy was used to make contacts to the sample using 5 mil Cu leads. Magnetic susceptibility measurements were performed using a Quantum Design coil extraction magnetometer. A 461 mg sample and a 50 kOe field were used for the measurements.

3. Results

The uncommon Ir_3Ge_7 structure-type, cubic $Im\bar{3}m$, has been variously described in terms of clusters [6] and lattice complexes [7]. Alternatively, it can be viewed as a framework of alternating corner-linked Ru_6Sn_8 capped-octahedral clusters and Ru_2Sn_4 flattened-octahedral clusters, such that the latter form their own three-dimensional sublattice (Fig. 1). About 40 compounds are known or assumed to have the Ir_3Ge_7 structure-type, and their total number of valence electrons per formula unit lie in the range 51 to 56 [8]. Among the assumed grouping, four ternary and quaternary compounds contain both Ru and Sn. The Ru–Sn distances determined for Ru_3Sn_7 fall in the middle of the observed range tabulated from the handful of

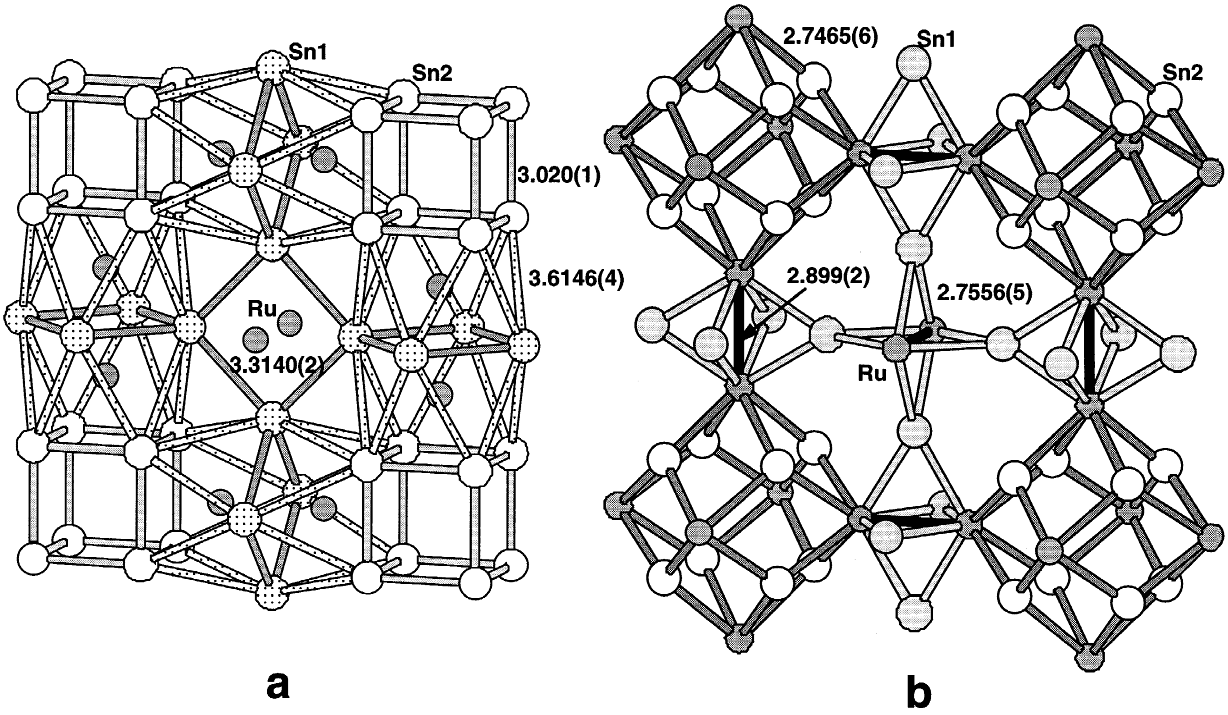

Fig. 1. Two different clinographic projections of the Ru_3Sn_7 crystal structure, showing about one half of the cell contents. In (a) near-neighbor Sn atoms are joined, which defines polyhedral cavities consisting of cubes, square anti-prisms, and tetrahedra. The Ru atoms occupy the square anti-prism. Not shown is an additional short Sn2 . . . Sn2 distance [2.886(1) Å] which links the Sn2 cubes along their body diagonals. In (b) near-neighbor atoms are joined which defines a framework of corner-linked clusters; see text for further discussion. Selected distances are labeled.

known Ru–Sn distances in intermetallics. The shortest interatomic separation, 2.7556(5) Å, is between Ru and Sn1, which creates its own three-dimensional network involving these atoms (Fig. 1(b)). This short distance is intermediate between the nearest-neighbor distances in Ru metal (2.65 Å) and Sn metal (2.81 Å). Contraction of the cell edge and changes in positional parameters are very slight upon cooling (Table 1).

Most of the Ir_3Ge_7-type compounds appear to be metallic; known exceptions are Re_3As_7 and Tc_3As_7 [8] which are semiconductors. The resistivity of Ru_3Sn_7 appears in Fig. 2. The magnitude of the resistivity varies from 72 μΩ cm at 300 K to 0.5 μΩ cm at 5 K. The resistivity is not consistent with conventional Bloch–Grüneisen behavior in that it is not linear at high temperature, but shows signs of impending ‘saturation.’ This behavior is reminiscent of A-15 superconductors such as Nb_3Sn, and is due to the presence of *d* orbitals near the Fermi energy into which the electrons can scatter [9–11]. No superconductivity was detected in Ru_3Sn_7 down to 2 K.

The magnetic susceptibility of Ru_3Sn_7 appears in Fig. 3. The most straightforward explanation of the data is that there are two contributions to the susceptibility: a temperature independent diamagnetic ‘core’ term, and a temperature dependent paramagnetic term arising from exchange enhancements within narrow *d*-like bands [12]. If this explanation is correct, a small amount of Fe substituted for Ru may lead to giant moments on the Fe atoms as occurs when Fe impurities are dissolved in Pd.

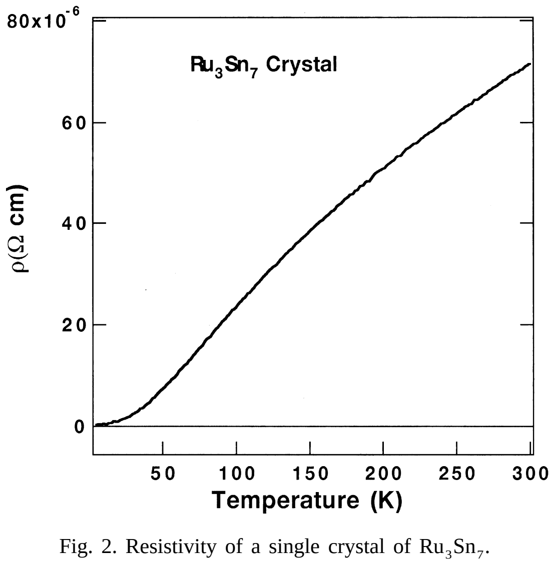

Fig. 2. Resistivity of a single crystal of Ru_3Sn_7.

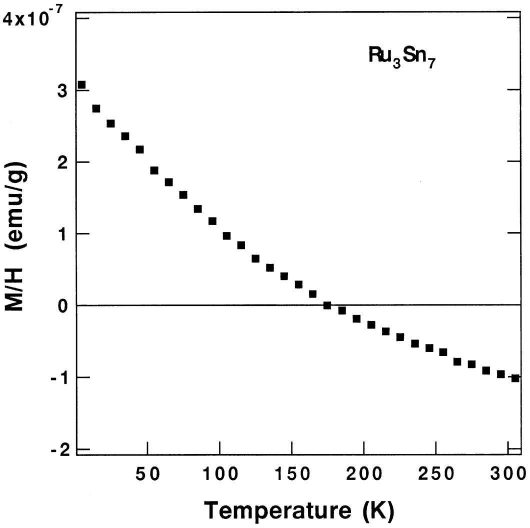

Fig. 3. M/H vs. temperature for Ru_3Sn_7.

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