

Structure and Properties of Yb₃Ge₅

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Single crystals of Yb₃Ge₅, grown from pure gallium or indium metal flux and investigated by means of CCD four-circle diffractometry, were consistent with the Th₃Pd₅-type of structure, displaying full order of vacancies and germanium atoms. From magnetic susceptibility and electrical resistivity measurements, performed on single-crystalline specimens, Yb₃Ge₅ was found to be an intermediate valent systems. © 2002 Elsevier Science (USA)

Key Words: Flux-grown single crystals of Yb₃Ge₅; crystal structure of Yb₃Ge₅ with Th₃Pd₅-type; magnetism and electrical conductivity; intermediate valent system

1. INTRODUCTION

Although rare earth metal disilicides and digermanides have gained some interest as electric contact materials in Si/Ge-waver-based electronic devices, as well as in optical fiber telecommunication because of sharply structured photoluminescence bands from rare earth intra-4*f*-shell transitions (1), there is still a serious lack (a) of reliable phase equilibria data for the Si(Ge)-rare earth systems, (b) of the crystal structure of the corresponding binary compounds (2, 3), and (c) of the physical properties of the intermediate phases. Rare earth metal/semiconductor interface formation and compounds have been investigated (4, 5) including ytterbium metal and subsequently two compounds have been recorded at the germanium-rich phase boundary: βYb₃Ge₅, as a high-temperature modification (> 935°C) with the defect AlB₂-type and αYb₃Ge₅, as a low-temperature modification with the Th₃Pd₅-type (2, 3). In a recent study, the authors established the phase relations in the relevant Si-rich part of the homologous Yb–Si system and confirmed the Th₃Pd₅-type structure for a flux-grown single crystal of Yb₃Si₅ (6). Physical properties, determined for

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Yb₃Si₅, revealed intermediate valence for ytterbium (6). With respect to the various types of Si/Ge-vacancy ordering recently encountered in rare earth disilicides and digermanides (7, 8), the present paper thus intends to provide the hitherto missing information on phase equilibria, crystal chemistry in combination with the physical behavior of Yb₃Ge₅ single crystal specimens.

2. EXPERIMENTAL

In a recent paper on Yb₃Si₅ (6) we presented details for the preparation of bulk alloys, the use of the Lebeau-method (9) for the growth of sizeable single crystal material from metal flux, a description of the X-ray techniques on powder and single crystal material as well as an outline of the physical measurements employed (magnetization, susceptibility and electrical resistivity).

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of Yb₃Ge₅ with the Th₃Pd₅-type

Whilst pure Zn or Ga-flux was less efficient in producing high-quality and sizeable single crystal material, in-flux reproducibly resulted in good quality and well-shaped single crystals (up to 0.25 × 0.5 × 5 mm³) of Yb₃Ge₅. Lattice parameters of the single crystals were perfectly in line with values obtained from arc melted and annealed bulk specimens as well as with values obtained from literature compilations (2, 3). Crystal quality control and inspection of crystal symmetry was accomplished by Weissenberg photographs. Single crystal X-ray intensity data for Yb₃Ge₅ were collected for a hemisphere in 242 images and a total exposure time of 157 h on a four circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite monochromated MoK α radiation ($\lambda = 0.071073$ nm). Orientation matrix and unit cell parameters were derived from the first 10 data frames using the program DENZO (10). Absorption correction was taken from program SORTAV

(10) ($\mu = 62.6 \text{ nm}^{-1}$). The structure was refined with the aid of the SHELXL-97 program (11).

Weissenberg photographs taken along [00.1] as well as the CCD representations of the reciprocal lattice planes [00.1] and [10.0] gave no indication of superstructures or deviation from a primitive hexagonal cell with $a \sim 0.68$ and $c \sim 0.41$ nm. The absence of systematic extinctions is fully compatible with the space group $P\bar{6}2m(D_{3h}^3, \text{No. 189})$ assigned in earlier investigations (7, 12, 13). Starting from the atomic arrangement in the Th₃Pd₅-type presented earlier (12), the refinement directly converged to residual values as low as 0.045. Refinement of the occupancies of all species proved the absence of any defects in the ordered atom arrangement. Results of the structural refinement are summarized in Table 1 including various residual values, anisotropic thermal parameters and interatomic distances.

TABLE 1
Structure refinement^a for X-ray single crystal data of Yb₃Ge₅(Th₃Pd₅-type)

Parameter/compound	Yb ₃ Ge ₅		
Lattice parameters (nm)	$a = 0.68495(2); c = 0.41765(1)$		
Space group; Z	$P\bar{6}2m$ — No. 189, origin at $\bar{6}2m, Z = 1$		
Structure type	Th ₃ Pd ₅ -type		
Density, $\rho_{X\text{-ray}}$ (Mgm ⁻³)	$\rho_{X\text{-ray}} = 8.63$		
Data collection; X-rays	Nonius Kappa CCD; MoK α_1		
2 Θ -range in deg	2.0–90.6		
Number of variables	12		
Full reflections in refinement	560 (540 > 2 σ) (meas. 3323)		
$R_1 = \sum I_o - I_c / \sum I_o$	0.045 ($I > 2\sigma$)		
R_1 (all data)	0.047		
Overall R_{merge}	0.081		
GOF	1.112		
Extinction (Zachariasen) EXTI	0.048		
Atom parameters			
	Yb in 3g ($x = 0.64144(9), 0, 1/2$)		
$U_{\text{eq.}}(U_{\text{iso}}) 10^2$ (nm ²)	0.0057(2) ^b		
	Ge1 in 3f ($x = 0.2590(3), 0, 0$)		
$U_{\text{eq.}}(U_{\text{iso}}) 10^2$ (nm ²)	0.0084(3) ^b		
	Ge2 in 2c (1/3, 2/3, 0)		
$U_{\text{eq.}}(U_{\text{iso}}) 10^2$ (nm ²)	0.0053(3) ^b		
Distances (nm) < 0.40000 nm;	Yb	4Ge2	0.30346
Standard deviation < 0.00006 nm		4Ge1	0.30303
		(2Ge1)	0.33500
	CN = 12(14)	4Yb	0.38140
		2Ge2	0.25760
		4Yb	0.30303
	CN = 8	2Yb	0.33500
		3Ge1	0.25760
		6Yb	0.30346

^a Crystal structure data were standardized using Program Typix -Structure Tidy (Ref. 18).

^b Anisotropic displacement factors (10² nm²) are: Yb: $U_{11} = 0.0034(2), U_{22} = 0.0061(2), U_{33} = 0.0067(2), U_{12} = U_{13}, U_{23} = 0.0017(1)$; Ge1: $U_{11} = 0.0038(5), U_{22} = 0.0038(5), U_{33} = 0.0091(7), U_{12} = U_{13}, U_{23} = 0.0019(2)$; Ge2: $U_{11} = 0.0033(6), U_{22} = 0.010(6), U_{33} = 0.0099(6), U_{12} = U_{13}, U_{23} = 0.0017(3)$.

A listing of the intensity data may be obtained from the authors on request. The simple crystallographic group-subgroup relationship among the high-temperature modification $\beta\text{Yb}_3\text{Ge}_5$ with the defect AlB₂-type and the low-temperature modification $\alpha\text{Yb}_3\text{Ge}_5$ with the Th₃Pd₅-type was already discussed (7). There is fine agreement with the results recently obtained for the isostructural silicide $\alpha\text{Yb}_3\text{Si}_5$ (6) as well as within the literature data presented, proving the fully ordered character of the defects in the AlB₂-type parent Si, Ge layers consistent with the description in the Th₃Pd₅-type.

Among the structure types within binary rare earths systems with silicon or germanium (7, 8), the Th₃Pd₅-type — although a most simple supercell of parent AlB₂-type — is the exception; it is only encountered for both isotopic compounds, Yb₃Si₅ and Yb₃Ge₅, as their low-temperature modification where intermediate valency of the ytterbium atom seems to be the characteristic and decisive feature (see below).

3.2. Physical Properties of Yb₃Ge₅

3.2.1. *Magnetism.* The molar magnetic susceptibility of single-crystalline Yb₃Ge₅, measured up to 800 K in a field of 0.5 T, is displayed in Fig. 1a. The magnitude of the susceptibility is small, and $\chi(T)$ exhibits rather weak temperature dependence with a broad shallow maximum around $T[\chi(\text{max})] = 500$ K, which resembles the behavior of intermediate valence systems. The pronounced tail at low temperatures is probably due to the presence of a small amount of magnetic impurities such as uncompensated Yb⁺³ ions on the crystal surface, as usually observed in intermediate valent materials. Accordingly, the experimental $\chi(T)$ data could be described by a formula

$$\chi(T) = \chi_{\text{ICF}}(T) + \chi_{\text{imp}}(T) + \chi_0, \quad [1]$$

where $\chi_{\text{ICF}}(T)$ is the susceptibility given by the interconfiguration fluctuation model (ICF) of intermediate valency (14), $\chi_{\text{imp}}(T)$ is the Curie-Weiss impurity contribution, and χ_0 stands for a sum of temperature-independent contributions, e.g., core-electron diamagnetism, conduction-electron paramagnetism and Van Vleck paramagnetism. In the scope of the ICF model, the susceptibility of an ytterbium-based compound with a nonmagnetic $4f^{14}$ ground state configuration and a magnetic $4f^{13}$ excited state configuration is represented by

$$\chi_{\text{ICF}}(T) = \frac{N\mu_{\text{eff}}^2 [1 - \nu(T)]}{3k_{\text{B}}(T + T_{\text{sf}})}, \quad [2]$$

where $\mu_{\text{eff}} = 4.54\mu_{\text{B}}$, T_{sf} is a spin fluctuation temperature and $\nu(T)$ is a temperature-dependent mean occupation of the ground state given by

$$\nu(T) = \frac{1}{1 + 8 \exp[-E_{\text{ex}}/k_{\text{B}}(T + T_{\text{sf}})]} \quad [3]$$

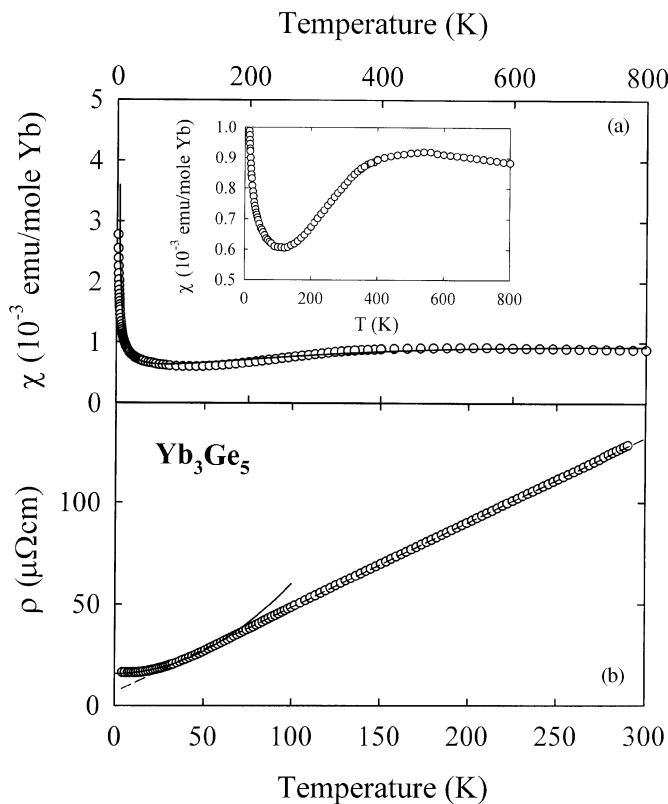


FIG. 1. (a) Temperature dependence of the molar magnetic susceptibility of Yb_3Ge_5 . The solid line is a fit of the experimental data to the formulas given in the text. (b) Temperature variation of the electrical resistivity of Yb_3Ge_5 , measured along the c -axis. The solid and dashed lines mark T^2 and T dependencies of the resistivity, respectively.

with an energy gap E_{ex} between the ground and excited states.

The least-squares fit of the experimental data to Eqs. [1–3] yielded the following values of the parameters: $T_{\text{sf}} = 769$ K, $E_{\text{ex}} = 3185$ K, $C_{\text{imp}} = 0.007$ emu K/mol, $\theta_{\text{imp}} = 1$ K and $\chi_0 = 0.8 \times 10^{-4}$ emu/mol. The calculated $\chi(T)$ is represented in Fig. 1a by a solid line. The agreement between the measured and theoretical curves is not as good as that obtained by the same method for Yb_3Si_5 (6), but the main features in the experimental $\chi(T)$ are satisfactorily described. The value of T_{sf} is close to the estimate (15) $T_{\text{sf}} = \frac{3}{2}T[\chi(\text{max})] = 750$ K. The large magnitude of E_{ex} clearly indicates that in Yb_3Ge_5 , the magnetic $4f^{13}$ configuration is quite distant from the nonmagnetic ground state. The ICF model gives for this compound at 4.2 K an effective valence of the ytterbium atom of only 2.1. With increasing temperature, the excited state becomes thermally populated and the valence increases, reaching a value of 2.5 at 800 K. Attributing the low-temperature tail in $\chi(T)$ to stable Yb^{3+} ions only, the impurity concentration ($n = C_{\text{imp}}/C_{\text{Yb}^{3+}}$ where $C_{\text{Yb}^{3+}} = \mu_{\text{eff}}^2/8$) is estimated to be as low as 0.3 at% Yb^{3+} ions per mole, i.e., it is much below the detection limit of X-ray diffraction.

3.2.2. Electrical Resistivity. The electrical resistivity of the Yb_3Ge_5 single crystal, measured along the c -axis, is shown in Fig. 1b. It shows a metallic-like behavior with the room temperature value of the order of $100 \mu\Omega\text{cm}$ and the residual resistivity ratio $\text{RRR} = \rho(290 \text{ K})/\rho(4.2 \text{ K})$ of about 8. Above 35 K, the resistivity is proportional to temperature (note the dashed line) indicating the predominance of phonon scattering processes. Below this temperature, $\rho(T)$ follows the equation

$$\rho(T) = \rho_0 + AT^2$$

with the parameters $\rho_0 = 16 \mu\Omega\text{cm}$ and $A = 0.004 \mu\Omega\text{cm}/\text{K}^2$. The T^2 behaviour of the resistivity is characteristic of a Fermi liquid (15), and thus being in line with the intermediate valent character of Yb_3Ge_5 , deduced from the magnetic data. From the Kadowaki–Woods relation $A/\gamma^2 = 10^{-5} \mu\Omega\text{cm} (\text{mol K}/\text{mJ})^2$ (16), between the coefficient A and the linear coefficient of the electronic specific heat, one estimates γ of about $20 \text{ mJ}/\text{mol}/\text{K}^2$. Such a moderately enhanced value of the Sommerfeld coefficient is typical for intermediate valence systems (15, 17).

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