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A Novel Intermetallic Compound, $CeCu_{1-x}Bi_2$

Jinhua Ye, Ying Kai Huang, Kazuo Kadowaki and Takehiko Matsumoto

National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305, Japan. E-mail: ye@nrim.go.jp

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Abstract

A novel intermetallic compound, $CeCu_{1-x}Bi_2$ ($x = 0.3$) [bismuth–cerium–copper (2/1/0.7)], has been synthesized by the bismuth self-flux method and its structure has been analyzed by single-crystal X-ray diffraction. The compound is found to have the $ZrCuSi_2$ structure type. This can be described as a layered structure in which two-dimensional Bi layers consisting of closely arranged Bi atoms in a square-lattice array and CeBiCu slabs formed by edge-sharing $CeBiCu_4$ distorted octahedra stack alternately along the [001] direction *via* Ce—Bi and Bi—Bi bonds, forming a three-dimensional network.

Comment

Recently, our search for strongly correlated electron systems has concentrated on the synthesis and growth of single crystals of ternary compounds in Ce–*T*–Bi (*T* = Cu, Au and Pt) systems. So far, we have succeeded in growing single crystals of $Ce_3Pt_3Bi_4$, $Ce_3Au_3Bi_4$, $CeAu_{1-x}Bi_2$ and $CeCu_{1-x}Bi_2$. Among these, the new ternary compound $CeCu_{1-x}Bi_2$ shows a sharp peak in magnetic susceptibility at about 12 K, indicating antiferromagnetic order. In addition, a stepwise magnetization as a function of magnetic field was observed below 12 K (Huang, Ye, Hirata & Kadowaki, 1995).

The X-ray diffraction analysis described in this work showed that $CeCu_{1-x}Bi_2$ is isotypic with $ZrCuSi_2$. The structure can be described as an intergrowth of Bi layers between CeBiCu slabs (Fig. 1). Bi atoms are located at the (100) and (010) face-centered positions of the tetragonal unit cell, and form sheets of Bi atoms in a square-lattice array. The CeBiCu slabs consist of $CeBiCu_4$ distorted octahedra with Ce and Bi atoms located at the two apices of the octahedra. These octahedra are connected to each other by sharing Cu—Cu edges, but the Ce and Bi atoms alternate on the apices. These two kinds of atomic layers stack alternately along the [001] direction *via* Ce—Bi and Bi—Bi bonds to form a three-dimensional network.

The large anisotropy in the displacement parameters for Bi2 and Cu, shown in Fig. 1, should be noted. It can be seen that Cu shows a larger displacement in the *xy* plane than in the *z* direction. In contrast,

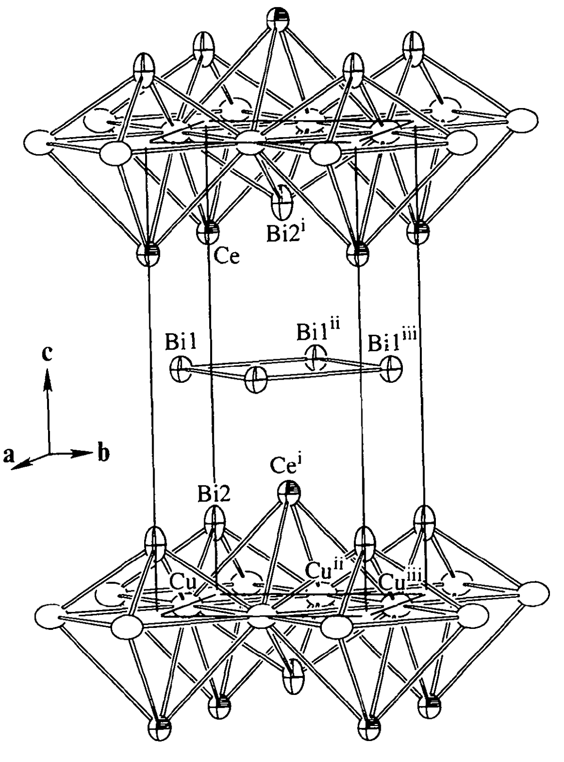

Fig. 1. *ORTEP*II (Johnson, 1976) illustration of $CeCu_{1-x}Bi_2$ (origin at 1/4, 1/4, 0 from center). Displacement ellipsoids are shown at the 90% probability level.

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Bi2 has a larger displacement along the z direction. The observed anisotropy can be understood in terms of copper deficiency at the Cu site ($2a$), such that the site occupancy is about 0.7. This deficiency was determined from composition analyses and is also consistent with the results of the structure refinement. The Cu atoms and vacancies are assumed to be randomly distributed at the $2a$ sites, since neither extra reflections nor streaking were observed in diffraction patterns recorded on an image plate. The disorder of the Cu atoms and vacancies at the $2a$ sites (distributed in the ab plane) leads to a larger displacement in the xy plane than in the z direction. Similarly, because of the existence of vacancies in the Cu plane (which is adjacent to the Bi2 atoms) the Bi2 atoms have the potential to approach the Cu plane, resulting in larger displacements along the z direction.

The Bi2—Cu distance [2.7093 (8) Å; Table 2] is extremely short compared with the sum of the metal radii (2.98 Å; Pearson, 1972), suggesting that the bonding between the Bi2 and Cu atoms is very strong. This strong bonding probably does not allow the Cu atoms to fully occupy the $2a$ sites, leading to the significant Cu deficiency. On the other hand, because of this strong bonding the Cu atoms are forced to vibrate more in the plane perpendicular to the Bi2 atoms in order to keep themselves far from the Bi2 atoms. Such movement of Cu atoms also explains the observed anisotropy in their displacement within the xy plane.

The strong bonding between the Bi and Cu atoms found in the present work is first such bonding to be observed. To our knowledge, no binary Bi–Cu intermetallic compound has been found up to now. As far as ternary intermetallic compounds involving Bi and Cu are concerned, several compounds in the Bi–Cu–S system are known (Bente & Kupcik, 1984), but none contain directly bonded Bi and Cu. Even in Ce_5CuBi_3 (Hohnke & Parthé, 1969), which contains the same elements as the title compound, the distances between the Bi and Cu atoms are so long (3.99 Å) they could not be considered as bonded.

The bond lengths between atoms within the two-dimensional layers, such as Bi1—Bi1^{ii} in the Bi layer or Bi2—Ce^{i} in the CeBiCu slab, are also slightly shorter than expected from the metal radii. This indicates relatively strong bonding within the layers. On the other hand, the interlayer distances, such as Bi1—Ce or Bi1—Bi2, are rather large, suggesting weak coupling between the layers. This is also consistent with the observed cleavage of the crystal along the (001) plane.

Focusing on the Ce atoms, which are known to play an important role in the magnetic properties of the compound, we find that these atoms form a pseudo body-centered lattice of tetragonal symmetry. As shown in Table 1 and Fig. 1, the Ce atoms are located at the $2c$ sites and can be viewed as forming two layers parallel to the ab plane. The two Ce-atom layers sandwich the strongly bonded Bi2 and Cu atoms, which form compact $BiCu_4$ pyramids. The bonding between the Ce and Cu atoms is rather weaker than that between the Bi2 and Cu atoms, and may be the reason for the approximate isotropy in the displacement parameters of the Ce atoms compared with the significant anisotropy observed for the Bi2 and Cu atoms. The distance between two Ce-atom layers located on opposite sides of a $CeBiCu_4$ octahedral slab and separated by $BiCu_4$ pyramids is $0.471c$ (4.604 Å), while the distance between two Ce-atom layers of different $CeBiCu_4$ octahedral slabs, which are separated by a Bi-atom layer, is $0.529c$ (5.168 Å). The similarity and yet slight difference of the locations of the Ce atoms from the body-centered lattice may give rise to the complicated magnetic properties at low temperature.

Recently, a series of isotypic compounds (RE)TSb$_2$ (RE = rare earth, T = Fe, Ni, Pd, Cu, Au or Ag) have been studied by Rogl's group (Leithe-Jasper & Rogl, 1994; Sologub, Hiebl, Rogl, Noel & Bodak, 1994; Sologub, Noel, Leithe-Jasper, Rogl & Bodak, 1995). From their structural studies, defect structures for some compounds have been reported. In $NdFe_{1-x}Sb_2$, no superstructure reflections due to long-range ordering of Fe atoms and vacancies were observed, but a weak streaking in the diffraction patterns was noticed, implying a tendency towards formation of a supercell. No such phenomenon was detected for $CeCu_{1-x}Bi_2$ in the present work. Further investigations of the annealing effects on the crystal structure and physical properties might be desirable in order to clarify these issues.

Experimental

Single crystals of $CeCu_{1-x}Bi_2$ were grown from a bismuth flux (Huang, Ye, Hirata & Kadowski, 1995) and have a well developed growth habit with a thin plate-like shape (size up to $6 \times 6 \times 0.3$ mm^3). The atomic ratio of Ce to Cu in the single crystals is about 3:2, as determined from scanning electron microscope energy-dispersive X-ray (SEM-EDX) analyses.

Crystal data

$CeCu_{0.71}Bi_2$
$M_r = 603.198$
Tetragonal
$P4/nmm$
$a = 4.555\,(2)$ Å
$c = 9.772\,(6)$ Å
$V = 202.7\,(1)$ Å^3
$Z = 2$
$D_x = 9.881$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 25.50$–$40.86°$
$\mu = 100.99$ mm^{-1}
$T = 293$ K
Prism-like
$0.10 \times 0.09 \times 0.05$ mm
Metallic

Data collection

Rigaku AFC-7R diffractometer
ω–2θ scans

420 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.13$

Absorption correction: ψ scans supplemented by a spherical correction
$T_{\min} = 0.0293$, $T_{\max} = 0.1066$
3427 measured reflections
698 independent reflections

$\theta_{\max} = 50.1°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 20$
3 standard reflections monitored every 100 reflections intensity decay: 14.8%

Refinement

Refinement on F
$R = 0.0483$
$wR = 0.0482$
$S = 1.16$
420 reflections
13 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.000075$
$\Delta\rho_{\max} = 6.19$ e Å^{-3}
$\Delta\rho_{\min} = -5.10$ e Å^{-3}

Extinction correction: Zachariasen (1968) type II Gaussian isotropic
Extinction coefficient: 415 (23)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Bi1	3/4	1/4	1/2	0.00967 (7)
Bi2	1/4	1/4	0.15015 (8)	0.01226 (8)
Ce	1/4	1/4	0.76444 (9)	0.0094 (1)
Cu†	3/4	1/4	0	0.0151 (4)

† Site occupancy 0.7055 (7).

Table 2. *Selected geometric parameters (Å, °)*

Bi2—Cu	2.7093 (8)	Bi1—Bi1$^{\rm ii}$	3.221 (2)
Bi2—Ce$^{\rm i}$	3.328 (2)	Bi1—Bi2	4.1079 (8)
Cu—Cu$^{\rm ii}$	3.221 (2)	Bi1—Ce	3.4446 (8)
Cu—Ce$^{\rm i}$	3.2382 (8)		
Bi1—Bi1$^{\rm ii}$—Bi1$^{\rm iii}$	90	Cu—Ce$^{\rm i}$—Cu$^{\rm iii}$	89.40 (3)
Cu—Cu$^{\rm ii}$—Cu$^{\rm iii}$	90	Bi1—Ce$^{\rm i}$—Bi1$^{\rm ii}$	55.75 (2)
Cu—Bi2—Cu$^{\rm ii}$	72.95 (2)	Bi1—Ce$^{\rm i}$—Bi1$^{\rm iii}$	82.79 (3)
Cu—Ce$^{\rm i}$—Cu$^{\rm ii}$	59.65 (2)		

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) y, x, z; (iii) $x, 1 + y, z$.

The crystals of $\mathrm{CeCu_{1-x}Bi_2}$ are brittle and yet very easily deformed. It was very difficult to cut a crystal into a favourable shape without destroying its single-crystal nature. In this study, a small fragment obtained by crushing big pieces of crystals was used for intensity measurements. Its single-crystal nature was confirmed in advance using a rotation camera. The space group was checked initially using a precession camera with an image plate instead of conventional X-ray film. After careful observation of various diffraction patterns, only $hk0$ reflections with $h + k = 2n + 1$ were recognized as being systematically absent, indicating the centrosymmetric space group $P4/nmm$. Neither long-range superstructure reflections nor streaking were observed.

During our preliminary experiments, the compound was found to be unstable in air. The single crystal was therefore sealed in a glass capillary for intensity-data collection. Even with such protection, the intensities of the standard reflections showed a linear decrease of 14.8% over the course of the data collection (114 h). A linear decay correction factor was applied to the intensity data before applying other corrections such as for Lorentz–polarization and absorption effects. Since the sample has an extremely high absorption coefficient (100 mm^{-1}) and is anisotropic in shape, an absorption correction based on ψ-scan measurement of several reflections was supplemented by a spherical correction.

Full-matrix least-squares refinement was carried out taking the $\mathrm{ZrCuSi_2}$ structure type (Sprenger, 1974; Thirion, Venturini, Malaman, Steinmetz & Roques, 1983) as the initial structure model, with Ce, Cu and Bi atoms placed at the Zr, Cu and Si sites, respectively. The least-squares refinement converged to $R = 0.060$ and $wR = 0.091$, but gave an abnormally large displacement parameter for the Cu atom (more than four times that of the other atoms). Refinement of the site occupancy for Cu immediately revealed a significant deviation from full occupancy to an occupancy of 0.7055 (7). (This result is in good agreement with the composition obtained from SEM-EDX analyses.) Simultaneously, the refinement resulted in reasonable displacement parameters for the Cu atom and led to further convergence of R to 0.0483 and wR to 0.0482. Refinement of the occupancies of other sites did not indicate any deficiency and R and wR were not further improved. The final difference electron-density map had maxima and minima of 6.19 and −5.10 e Å^{-3} in the vicinity of the Bi atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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