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Structural transition and volume compression of CeBi up to 20 GPa

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Résumé. — La diminution du volume de CeBi a été mesurée à température ambiante jusqu'à 20 GPa par diffraction X dans une cellule à enclumes de diamant. En dessous de 13 GPa, la structure de CeBi reste de type NaCl avec un module de compression égal à 49,6 GPa qui est inférieur à celui rapporté pour LaBi (55 GPa). Cette diminution est attribuée à une augmentation continue de la valence du cérium. Une transition cristallographique se produit à $P = 13$ GPa. Deux structures avec des volumes de maille très voisins coexistent alors : une structure quadratique (groupe d'espace $P 4/m m m$, $Z = 1$) et une structure cubique de type CsCl. Les modules de compression des phases haute pression sont nettement plus élevés que celui de la phase de type NaCl. Le faible changement de volume à la transition cristallographique est attribué à une diminution de la valence du cérium ou à une réduction du mélange p-f, dues à l'augmentation de la distance cérium-bismuth dans les deux phases haute pression.

Abstract. — The compression curve of CeBi up to 20 GPa was measured at room temperature by x-ray diffraction in a diamond anvil cell. Below 13 GPa, CeBi maintains its cubic structure of the NaCl-type with a bulk modulus $B_0 = 49.6$ GPa, smaller than that reported for LaBi ($B_0 = 55$ GPa). This anomalous lowering is attributed to a continuous increase of the cerium valence.

At $P = 13$ GPa, CeBi undergoes a crystallographic transition. Two high pressure structures with close unit-cell volumes have been found to coexist : a tetragonal structure (space group $P 4/m m m$, $Z = 1$) and a cubic structure of the CsCl-type. The bulk moduli of the high pressure phases are markedly higher than that of the NaCl-type phase. The small volume change at the crystallographic transition is attributed to a decrease of the cerium valence or a lowering of the p-f mixing due to the larger cerium-bismuth distances in both high pressure phases.

1. Introduction.

The cerium monopnictides CeX ($X = N, P, As, Sb, Bi$), with the NaCl structure, exhibit very unusual magnetic properties [1] resulting from the presence of the 4f level close to the Fermi energy (E_F) which is actually a general feature of anomalous rare earth systems such as the cerium ones. In cerium monopnictides, Baer *et al.* [2] have shown by XPS measurements that the 4f level is close to or at the Fermi level in CeN, yielding then a mixed valence state, but moves towards higher binding energy from CeP to CeBi. In CeP the 4f¹ level was found to be 0.4 eV below E_F and actually

a pressure of 10 GPa [3] is large enough to induce an electronic transition associated with a large volume reduction ($\sim 8\%$). A similar valence change was expected in CeAs, but Werner *et al.* [4] have shown that CeAs undergoes only a simple structural transition from the NaCl to the CsCl-type structure at $P \sim 15$ GPa. In CeSb and CeBi the 4f electron is more tightly bound and the magnetic properties are expected to become more classical. In fact, CeP and CeAs are simple antiferromagnets whereas CeSb and CeBi exhibit unusual magnetic properties such as a very small crystal field splitting, a very large magnetic anisotropy and a complex magnetic phase diagram. These properties actually result from the semi-metallic character of CeSb and CeBi. Band calculations [5] indicate that a small amount of p-holes exists at the

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zone centre while the electrons of 5d (T_{2g}) character are concentrated at the zone boundary. The mixing interaction between the 4f electron and the anion p-band is then much stronger as was shown by Kasuya's group [6] and so CeSb and CeBi exhibit anomalous properties although the 4f electrons are further away from the Fermi level. The anomalous transport properties of cerium monpnictides are in some sense similar to those of compounds which exhibit a Kondo-like behaviour, the origin being in this case, the mixing of f electrons with 5d conduction electrons.

The volume dependent Kondo interaction has been shown [7, 8] to give rise to a negative contribution to the free energy and so to a lowering of the bulk modulus. An applied pressure can then induce an electronic transition either of second or first order depending on temperature. In CeTe, such an interaction has been claimed [9] to be the origin of the continuous electronic transition induced by pressure in the NaCl-type phase. Moreover it explains the reentrant behaviour at the crystallographic transition because the cerium-tellurium distance is larger in the CsCl high-pressure phase.

In CeSb and CeBi, which show pronounced mixing effects at normal pressure, a lowering of the bulk modulus is expected. Actually only a very small decrease of the bulk modulus due to mixing effects has been found in CeSb [10]. However the stronger p-f mixing in CeBi should give rise to a larger effect and the P - V relationship should then reveal an anomalous behaviour. Therefore an x-ray powder diffraction investigation of CeBi under pressure has been undertaken and the results are reported in this paper.

2. Experiments.

The x-ray powder diffraction experiments under high pressure have been carried out in a diamond anvil cell previously described [9, 10]. A collimated ($\varnothing = 0.15$ mm) Zr-filtered x-ray radiation produced by a fine focus molybdenum tube was used. The diffraction patterns were recorded on planar photographic films and corrections for their shrinkages were calculated from marks made at a known length. The sample to film distance was approximately 25 mm. Good diffraction patterns were recorded within 24 hours.

The CeBi compound was prepared in a single crystal form at E.T.H. Zurich using a mineralization method [11]. It was then crushed into powder and mixed with silicon grease, the pressure transmitting medium, and cesium chloride or gold acting as pressure standards. The pressure transmitting medium used here actually protects the sample against moisture. Pressure was calculated from the observed lattice parameter of the pressure standard by using the equation of state as proposed by Decker [12] for CsCl or assuming a Birch's equation of state for gold with a bulk modulus and its first pressure derivative at normal pressure calculated from the available volume compression data [13, 14].

3. Results.

In the lower pressure range, when increasing pressure, only the characteristic lines of the NaCl-type structure were observed. As the scattering factors of cerium and bismuth are very close only the diffraction lines with even indices appeared in the x-ray diffraction patterns. In all cases, the (200), (220) and (400) lines were observed; however, with a longer exposure time the (422) line appeared clearly and sometimes the weaker (222) and (420) lines were also detected. As seen in figure 1, the volume of this NaCl-type phase decreases smoothly with pressure up to $P \approx 13$ GPa. Above $P = 13$ GPa, the diffraction pattern is completely transformed indicating that a new high pressure phase has emerged. With increasing pressure, the simultaneous presence of the low and high pressure phases has not been observed; so, if they coexist, it must be in a small pressure range (~ 0.5 GPa).

A run without any pressure marker has been performed in order to determine unambiguously the diffraction pattern of the high pressure structure. In this case, six diffraction lines were clearly recorded but the two lines at large angle were definitely broader. The pattern appeared as being very similar to the one previously reported for the high pressure phase of CeSb [10], therefore a similar tetragonal structure was attributed to the high pressure phase of CeBi. In the

Fig. 1. — Relative volume of CeBi as a function of pressure. Filled symbols : increasing pressure, open symbols : decreasing pressure. The lines show least square fits to the Birch's equation of state. (—●○ NaCl-type structure; —■□ CsCl-type structure; —◆◇ tetragonal structure.)

unit cell the atoms have the following special positions : Ce : (0, 0, 0); Bi : (1/2, 1/2, 1/2) and the proposed space group is $P4/m\,mm$.

At about $P = 11$ GPa when pressure is decreasing, the cell constants of this tetragonal structure are $a = 3.993 \pm 0.003$ Å and $c = 3.350 \pm 0.01$ Å (Fig. 2). Such an unit cell can contain only one molecule in order to get a reasonable value for the density. The ratio $c/a = 0.84$, is slightly larger than observed for the high-pressure phase of CeSb ($c/a = 0.82$). The agreement between both the calculated and observed interplanar distances, the computed and visually estimated intensities is excellent (Table I). Actually the two broad lines correspond both to two close lines.

Three extra lines appeared at high pressure with a variable intensity in the different experimental runs. They have been attributed to an additional high pressure phase of CeBi which is present in a variable amount according to the experimental conditions and history. This seems very likely because these three additional lines can be indexed in a cubic lattice of the CsCl-type (Table II). Its volume is very close to that of the tetragonal structure; the difference is only about 0.7 % of the initial volume. The agreement between both the calculated and observed interplanar distances, the computed and visually estimated intensities is also quite excellent.

Therefore in CeBi under high pressure, a tetragonal and a cubic phases coexist above the transition, with quite close volumes over the whole pressure range investigated. With decreasing pressure these two phases are stable down to $P = 4.5$ GPa below which they progressively transform back into the low pressure phase of the NaCl-type. It is nearly completed only below 2 GPa.

The simultaneous presence of two structures with close volumes is not uncommon under high pressure and is well known to occur for cerium metal itself.

Fig. 2. — Pressure dependence of the lattice constants and the c/a ratio for the high pressure tetragonal structure of CeBi.

Table I. — X-ray diffraction data for the high pressure phase of CeBi with the tetragonal structure. At $P \simeq 11$ GPa, $a = 3.993 \pm 0.003$ Å, $c = 3.350 \pm 0.01$ Å, $c/a = 0.839$, $Z = 1$, $V/Z = 53.41$ Å³.

$h\ k\ l$	d obs. (Å)	d cal. (Å)	I cal.	I obs.
1 1 0	2.821	2.823	64	75
1 0 1	2.571	2.566	100	100
2 0 0	1.996	1.996	25	25
0 0 2	—	1.675	7	—
2 1 1	1.575	1.576	50	50
1 1 2	1.432	1.441	19	15
2 2 0	1.412	1.412	9	10
2 0 2	1.271	1.283	13	15
3 1 0	1.263	1.263	13	15
3 0 1	—	1.237	12	—

Table II. — X-ray diffraction data for the high pressure phase of CeBi with the CsCl-type structure. At $P \simeq 13.7$ GPa, $a = 3.739 \pm 0.003$ Å, $Z = 1$, $V/Z = 52.28$ Å³.

$h\ k\ l$	d obs. (Å)	d cal. (Å)	I cal.	I obs.
1 1 0	2.644	2.644	100	100
2 0 0	1.879	1.870	19	15
2 1 1	1.542	1.526	42	25
2 2 0	—	1.322	14	—
3 1 0	—	1.182	19	—

4. Discussion.

4.1 THE CUBIC PHASE OF THE NaCl-TYPE. — Below $P = 13$ GPa, the volume of CeBi decreases smoothly with pressure and its variation can be represented, as shown in figure 1, by an equation of state as proposed by Birch [15],

$$P = \frac{3}{2} B_0 \left[\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right] \times \left[1 - \frac{3}{4} (4 - B'_0) \left(\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right) \right]$$

where B is the bulk modulus, B' its first pressure derivative and V the volume; the subscript zero refers to values at normal pressure. A least square fit of the experimental data to this equation yields : $B_0 = 49.6 \pm 1$ GPa, $B'_0 = 2.10 \pm 0.2$. In purely ionic compounds the bulk modulus varies with the unit cell volume as V^{-1} or $V^{-4/3}$ according to different theories, and in purely covalent or metallic compounds as $V^{-5/3}$ [16, 17]. The results are generally displayed in a log-log plot. Actually it appears that the bulk modulus

of ionic isostructural monochalcogenides of rare earths or alkaline earths varies in a large volume range (Fig. 3) as $V^{-3.4/3}$.

A few data have been reported for rare earth mononictides [3, 4, 10]; they are also shown in figure 3. The bonding in these compounds is predominantly, but not fully, covalent excepted in nitrides where it is rather ionic. Deviations from a single power law are then possible; but within a particular pnictide series the bonding is not expected to change when going from lanthanum to cerium. Then the cerium compound which has the lower volume should have the higher bulk modulus. This increase of the bulk modulus for CeBi with respect to LaBi is not observed, actually the opposite result has been found. The difference is not large but certainly outside the experimental uncertainties. This lowering of the bulk modulus of the cerium compound is of the same order of magnitude as that found for tellurides :

$$\begin{aligned} \text{CeBi} : 49.6 \text{ GPa}; \quad \text{LaBi} : 55 \text{ GPa} \\ \text{CeTe} : 53 \text{ GPa}; \quad \text{LaTe} : 61 \text{ GPa} . \end{aligned}$$

The first pressure derivative of the bulk modulus of CeBi is close to the value found for other cerium mononictides CeAs : 2.6; CeSb : 2.5; CeBi : 2.1. The value of 13.6 found for CeTe [9] is quite anomalous and is a strong additional indication that cerium undergoes a continuous electronic transition in this compound under high pressure. Although the pressure derivative of the bulk modulus of CeBi does not show any abnormal value, CeBi exhibits probably the same behaviour because the bulk modulus and its pressure derivative have both low values.

Fig. 3. — Bulk moduli as a function of the unit cell volume in a log-log scale. The lower line corresponds to rare earth or alkaline earth ionic monochalcogenides; the data for cerium mononictides show deviations from a single power law.

The magnetic properties of CeBi at normal pressure have been accounted for by the mixing of 4f electrons with the valence band electrons (p-f mixing) [1]; this mixing originates from the existence of a small amount of p-holes due to the semi-metallic character of CeBi. This p-f mixing will lower the bulk modulus as the Kondo-like coupling does, because they have the same origin, the Kondo coupling being only a part of the mixing interaction.

The bulk modulus of CeBi has a significantly lower value than that of LaBi as expected for a mixing interaction which becomes stronger as the volume decreases. Under an applied pressure this mixing interaction gives rise to an additional shrinkage of the volume which can actually be interpreted as a continuous change of the valence of cerium. To estimate this effect it is needed to calculate the volume reduction of a hypothetical compound having the same initial volume as CeBi but without the p-f mixing interaction. In these conditions, the bulk modulus would be equal to that of LaBi multiplied by the 5/3 power of their relative volumes which gives a value of 58 GPa. Assuming the first pressure derivative to be equal to 2.5, as found for CeSb or LaSb, the volume of this hypothetical CeBi is about 3.3 % larger than the actual CeBi at $P = 13$ GPa. By using then the usual ionic radii [9, 18], we deduce from the Vegard's law that the valence of cerium just prior to the transition is about 3.25, but use of the usual value of four for B'_0 leads to a valence equal to 3.34.

In the NaCl-type phase, just below $P = 13$ GPa, the pressure-volume results are then consistent with a mean valence for cerium of about 3.3.

4.2 THE HIGH-PRESSURE PHASES. — The tetragonal structure found at higher pressures (space group $P 4/m m m$, $Z = 1$) is quite uncommon among equi-atomic binary compounds. At normal pressure, only AuCu displays this peculiar structure but the c/a ratio is then very close to unity. Under high pressure CeSb and CsI transform into this tetragonal structure with a similar c/a ratio. This structure can be looked upon as being a special case of the tetragonal structure of the PH_4I -type which is adopted by BaO under high pressure [19]. The atoms are then in the following positions : Ba : 0, 1/2, u and 1/2, 0, u ; O : 0, 0, 0 and 1/2, 1/2, 0; ($u = 0.40$, $Z = 2$).

Using the new parameters $a' = a\sqrt{2}$, $c' = c$, $u' = 0.50$ and $Z' = 2$, CeBi can also be seen as belonging to the structure of the PH_4I -type which is thought to be adopted preferably to the CsCl-type (B_2) structure by less ionic compounds. This is actually the case for CeBi and CeSb as compared to CeAs.

The smooth volume variations of the two high-pressure phases can be also tentatively described by the Birch's equation of state. In both cases, there is a third unknown parameter, the volume that the high pressure phase would have at normal pressure. For the structure of the CsCl-type the least square fit

of the data yields directly :

$$B_0 = 77.2 \pm 3 \text{ GPa}, B'_0 = 2.93 \mp 0.4, \\ \frac{V_{0\text{CsCl}}}{V_{0\text{NaCl}}} = 0.860.$$

For the tetragonal phase, $V_{0\text{tetra}}/V_{0\text{NaCl}}$ is determined by extrapolation of the high pressure data (Fig. 2). In these conditions the following values are obtained :

$$B_0 = 68.3 \pm 3 \text{ GPa}; B'_0 = 2.86 \mp 0.4; \\ \frac{V_{0\text{tetra}}}{V_{0\text{NaCl}}} = 0.867.$$

Let us examine closely the volume difference at normal pressure between the NaCl and the CsCl-type phases. In that case the change of the coordination number is then well defined and the cerium-bismuth distance in the CsCl phase can be calculated from its value in the NaCl phase providing ionic radii are adequate and cerium retains its trivalent state. Under these conditions, we obtain :

$$d_{(\text{Ce}-\text{Bi})\text{CsCl}} = d_{(\text{Ce}-\text{Bi})\text{NaCl}} + r_{\text{Ce}^{3+}\text{vIII}}^3 - r_{\text{Ce}^{3+}\text{vI}}^3 = 3.385 \text{ \AA}.$$

This value gives $V_{0\text{CsCl}}/V_{0\text{NaCl}} = 0.85$, in good agreement with the experimental value 0.867. The volume decrease between the two structures is of the same order as usually found for such structural transitions ($\sim 10\text{-}15\%$).

The volume variation at the NaCl $\rightarrow$ tetragonal transition is slightly less, but still of the same order. This is in agreement with the results reported for the NaCl $\rightarrow$ PH_4I structural transition in BaO [29] where the volume jump at the transition was found to be close to the value observed when the CsCl-type structure is obtained. At normal pressure the volumes of the CsCl and tetragonal phases are in excellent agreement

with the hypothesis of cerium being in a trivalent state in both phases.

It has been often outlined that the transition of the γ - α type in cerium compounds does occur when the Ce-Ce distance is close to 3.4 Å. Such a small distance is not observed in the CsCl-type structure over the whole pressure range investigated but is already found at $P = 8$ GPa in the tetragonal structure; nothing special was then observed.

4.3 THE CRYSTALLOGRAPHIC TRANSITION. — With increasing pressure, the crystallographic transition takes place at $P = 13$ GPa; the volume collapse is very small ($\sim 5.5\%$) for such a structural change which corresponds to an increase of the coordination number from six to eight, actually values of 10-15 % are expected. The difference in volume between the NaCl and the CsCl (or tetragonal) structures decreases progressively with pressure. This behaviour comes from the low values of the bulk modulus and its first pressure derivative in the NaCl phase as compared with the high pressure phases.

At the transition pressure, the cerium-bismuth distance increases by as much as 0.20 Å when going from the NaCl to the CsCl-type phase as compared with 0.11 Å in CeAs for the same structural transition [4], which is the expected value if cerium remains in a stable trivalent state.

Such a large increase of the cerium-bismuth distance can be analysed in the same way as in CeTe [9]. There are two main effects : a lattice effect due to the increase of the coordination number from six to eight and an electronic effect. The variation of the cerium-bismuth distance can be interpreted as a variation of the cerium radius (or cerium valence) because the anionic radius is independent of the crystal structure [18]. Assuming a linear relationship between valence and lattice parameter it is possible to estimate the variation of the valence across the NaCl $\rightarrow$ CsCl transition. The variation of the cerium radius at the transition is equal to 0.20 Å and is given by :

$$r_{\text{Ce}^{3+\delta}\text{vIII}}^3 - r_{\text{Ce}^{3+\varepsilon}\text{vI}}^3 = r_{\text{Ce}^{3+}\text{vIII}}^3 - r_{\text{Ce}^{3+}\text{vI}}^3 + \varepsilon(r_{\text{Ce}^{3+}\text{vI}}^3 - r_{\text{Ce}^{4+}\text{vI}}^3) - \delta(r_{\text{Ce}^{3+}\text{vIII}}^3 - r_{\text{Ce}^{4+}\text{vIII}}^3)$$

where

$$r_{\text{Ce}^{3+}\text{vI}}^3 = 1.034 \text{ \AA}, \quad r_{\text{Ce}^{3+}\text{vIII}}^3 = 1.14 \text{ \AA}, \quad r_{\text{Ce}^{4+}\text{vI}}^3 = 0.85 \text{ \AA}, \quad r_{\text{Ce}^{4+}\text{vIII}}^3 = 0.97 \text{ \AA}$$

r_{Ce} is the ionic radius of cerium with different coordination numbers (roman figure) and oxidation states (superscript) [9, 18]; ε and δ are the proportions of Ce^{4+} in the NaCl and CsCl-type phases. This relation gives $\delta = \varepsilon - 0.5$; so the valence of cerium decreases when CeBi undergoes the NaCl $\rightarrow$ CsCl phase transition, leading to a reentrant behaviour.

An other estimate of the valence change occurring at the transition can be obtained from the direct comparison of CeBi with CeSb or LaSb which undergo

the same NaCl $\rightarrow$ tetragonal transformation under high pressure [10] and where no electronic transfer takes place. At this transition, the Ce-Sb and La-Sb distances increase by an amount of 0.17 Å whereas in CeBi, the increase is equal to 0.24 Å. If we assume that the difference between these two values comes from an electronic effect and that there is a linear relationship between valence and ionic radius, these values lead to a decrease of the valence at the transition by about 0.4.

Therefore both estimates indicate that the valence decreases by about 0.4-0.5 at the NaCl $\rightarrow$ CsCl or NaCl $\rightarrow$ tetragonal transition, giving rise to a reentrant behaviour. This valence change is somewhat overestimated because the higher bulk moduli of the high-pressure phases have not been taken into account; usually an increase of the bulk modulus leads to a valence change smaller by about 0.1 [20]. So, it is reasonable to consider that in CeBi, at the crystallographic transition, the valence of cerium goes back by approximately 0.3-0.4. This value compares quite well with the increase, 0.25-0.35, induced by pressure in the NaCl-type phase. Therefore, above the transition, the valence of cerium is equal to three or very close to in both phases and in the NaCl-type phase, pressure induces a continuous valence change.

5. Conclusion.

The pressure-volume relationship of CeBi has been determined up to $P = 20$ GPa by x-ray diffraction using a diamond anvil cell. At $P = 13$ GPa, the NaCl-type phase transforms into both a tetragonal and a CsCl-type phases. The compression data of the different phases have been fitted to the Birch's equation of state and values for the bulk moduli and their first pressure derivatives have been deduced. The bulk modulus of the low-pressure phase (NaCl-type) of CeBi is smaller than that reported for LaBi; its first pressure derivative has also a somewhat low value.

At normal pressure the estimated volumes of the CsCl-type and tetragonal phases are in excellent agreement with the assumption of cerium being trivalent as in the NaCl-type phase.

Under pressure, the compression of the NaCl-type phase is larger than expected from a pure lattice contribution. The additional compression can be attributed either to a partial and continuous increase of the valence of cerium or to a mixing effect which increases as the volume decreases; these two considerations are somewhat similar. However, the increase of the valence is rather large, about 0.3, in a limited pressure range and indicates that, already at normal pressure cerium is in, or very close to, an intermediate valence state. No evidence of this fact has been reported up to now but the magnetic properties at normal pressure are well accounted for by large p-f mixing effects.

The small decrease of the volume at the crystallographic transition and the resulting large increase of the cerium-bismuth distance has been attributed to a discontinuous reentrant behaviour of the cerium valence at the transition: the valence decreases then by about 0.3-0.4. It follows that just above the transition, in both high pressure phases the cerium is in a trivalent state or close to. The physical origin of this behaviour is the decrease of the mixing interaction due to the larger Ce-Bi distance induced by the crystallographic transformation.

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