High-Pressure Transformations of NdI₂

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A p,T-diagram for NdI₂ is reported. The transformation from an SrBr₂-type arrangement to a Ti₂Cu-type structure takes place between 10 and 20 Kb, with a negative slope for the phase boundary. Due to kinetic hindrance at lower temperatures, an intermediate phase with a CaF₂-type arrangement can be detected by *in situ* X-ray investigations. A mechanism for the transformation is proposed. Structural parameters are refined by Rietveld analysis, and the compressibilities of the phases are given.   © 1992 Academic Press, Inc.

Introduction

The diiodides of La, Ce, and Pr crystallize in a Ti₂Cu-type structure (among others) which has so far only been found for intermetallic compounds. This tetragonal structure is isopuntal with MoSi₂, however, it has significantly larger c/a ratios, and this results in a more layer-like arrangement, which is shown in Fig. 1. The distances between the cations in the (001) plane are only little larger than those in the corresponding metal structures. The anisotropic metallic conductivity of these phases is explained by the good overlap of the 5d orbitals into which f-electrons could be promoted and delocalized (*1*).

In an earlier paper (*2*) one of us has reported that NdI₂ crystallizing in an SrBr₂-type structure can be transformed to the same Ti₂Cu-type arrangement at higher pressures. This transformation merits special attention since it is an interesting variant among insulator–metal transitions, and we have therefore investigated it more closely to get an insight into the mechanisms governing it.

Experimental

NdI₂ was prepared by the reaction of anhydrous NdI₂ with Nd metal (10% more than the stoichiometric amount) in Ta ampules which were sealed in evacuated silica tubes. The mixture was first reacted at 900–950°C for 1 day and quenched. It was then equilibrated at temperatures between 500 and 700°C for several days to improve crystal quality. All manipulations of the synthesis and of subsequent high-pressure investigations were performed under an Ar atmosphere.

The high-pressure phase was synthesized in a belt-type apparatus in boron nitride containers in a graphite tube as heating element. Typical conditions are 20–40 Kb at 400–500°C for 1–2 hr to attain a complete transformation. After quenching by an abrupt cut of the voltage and subsequent release of pressure, the black product can
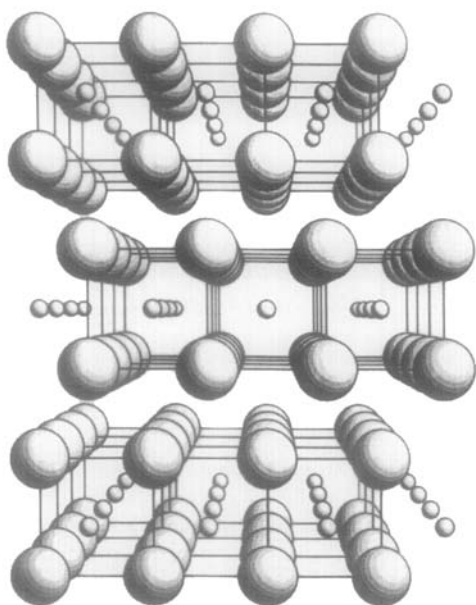
FIG. 1. Structure of the high-pressure phase NdI_2-II (Ti_2Cu-type) viewed along [100].

be isolated in a glove box. This high pressure phase remains metastable at ambient pressures. It is converted to the thermodynamically stable form by heating up to 300°C. It is evident from the phase diagram given in Fig. 2 that other conditions of transformation are possible.

In situ X-ray experiments were performed using a diamond anvil device (culet diameter 0.6 mm) of the Keller–Holzapfel type (*3*) with $MoK_{\alpha1}$ radiation (Quartz monochromator). An internal heating element was added in the form of a small resistance heater surrounding the diamonds. The powdered specimen was contained in a small hole (diameter 0.3 mm) drilled in an Inconel gasket (0.3 mm thick). Because of the lower absorption coefficient, NaF was used as an internal pressure standard after calibrating it against CsCl and NaCl in the same experimental setup (*4*). (At temperatures above 230°C the lines of NaI could be detected which formed by reaction of NdI_2 with NaF.)

The diamond anvil cell was mounted in a HUBER eulerian cradle where it was rocked in φ and χ during the steps of the measurement to improve the orientation statistics of the crystallites and to avoid reflections from the diamonds. A position-sensitive proportional counter (Braun) covering 8–10° in Θ simultaneously was moved in steps of 0.01° Θ, and this movement was taken into account in the data collection in a multichannel analyser. The spatial resolution and the "linearity" of the counter was calibrated by correlating defined step motor movements with the position of the peak of a sharp Si reflection evaluated by a profile fitting procedure from a powder diagram (specimen mounted in a 0.01-mm capillary, transmission geometry). Diagrams were taken in the range $5°<2\Theta<30°$. This angle-dispersive setup shows a considerably better performance and resolution than the energy-dispersive ones usually used. The data points to establish the p,T-diagram were taken in series where either the pressure was increased at constant temperature or the temperature at constant pressure. Since the back transformation from the high-pressure phase is kinetically hindered, subsequent experiments were always done on increasing the pressure. A new series always began with freshly filled gaskets.
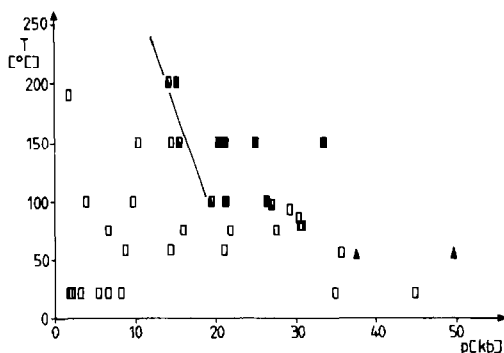

FIG. 2. p,T-diagram of NdI_2 (open rectangles NdI_2-I, filled rectangles NdI_2-II, filled triangles NdI_2-III).

X-ray investigations of the normal phase and the quenched high-pressure phase were made with $CuK_{\alpha 1}$ radiation (Ge monochromator) in Guinier-type cameras where the specimens were sealed in glass capillaries. Structural data were refined by a Rietveld procedure with the program from Wiles *et al.* (5).

Results and Discussion

The p,T-diagram of NdI₂ determined by X-ray *in situ* measurements is given in Fig. 2. At temperatures above 150°C the transformation from the SrBr₂-type structure to a Ti₂Cu-type arrangement is sufficiently activated. The fields of existence of NdI₂-I and NdI₂-II are separated by a boundary line with negative slope, indicating an increase in entropy during the transformation to the high-pressure phase. Extrapolating this line, one would expect a similar transition at ambient pressures at about 500°C. However, such a reaction has not been observed yet. At lower temperatures the field of existence of the low-pressure phase seems to extend to higher pressures. It can be assumed that this is due to a kinetic hindrance of the transformation and does not reflect a system governed by thermodynamics. In this low-temperature region a new phase NdI₂-III is detected at higher pressures. Its existence could only be conjectured from the unusual intensities of some reflections of NdI₂-I, since all its reflections, in the range which could be examined, coincide with those of the compressed low-pressure phase. From these "reflections" a cubic cell with a = 7.688 Å (extrapolated to ambient pressures) could be inferred, and a calculation of intensities on the basis of a fluorite-type lattice agreed fairly well with those observed. Such an arrangement can very well be assumed as an intermediate step in a transformation mechanism (see below).

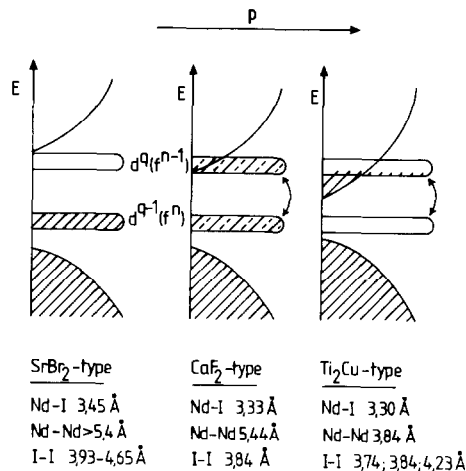The new CaF₂-type high-pressure phase combines features of NdI₂-II and of the

FIG. 3. Comparison of features of the band structure for the three NdI₂ polymorphs.

SrBr₂-type	CaF₂-type	Ti₂Cu-type
Nd-I 3.45 Å	Nd-I 3.33 Å	Nd-I 3.30 Å
Nd-Nd >5.4 Å	Nd-Nd 5.44 Å	Nd-Nd 3.84 Å
I-I 3.93-4.65 Å	I-I 3.84 Å	I-I 3.74; 3.84; 4.23 Å

phase stable at ambient pressures. Extrapolating the lattice constants to ambient conditions for better comparison we find Nd-I distances of 3.33 Å, which come close to those found in NdI₂-II. The I–I distances (3.84 Å) also indicate a drastic change in bonding character. However, there is no short Nd–Nd contact. NdI₂-III is probably only a semiconductor, whereas metallic conduction could be established for NdI₂-II.

The situation may be described in the terminology of band structures (Fig. 3). In NdI₂-I the narrow bands associated with the d^0f^n and the d^1f^{n-1} configuration of the metal atoms are situated within a large gap. A change of configuration by some activation process would not result in any change of physical properties. The same is true for NdI₂-III, where Nd valence electrons may have been promoted to I–I bonding states. (This would explain short Nd–I and I–I distances.) The band gap is still too large to be overcome by thermal activation. It may be considerably reduced in the phase NdI₂-II, since band dispersion increases when distances decrease. The d^1f^{n-1} band will then have energies in the range of the conduction

TABLE I

CONDITIONS AND RESULTS OF RIETVELD REFINEMENTS FROM DATA TAKEN
AT AMBIENT CONDITIONS

	NdI_2-II	LaI_2
Ti_2Cu type	Space group $I4/mmm$	$M2a$ (0,0,0) $I4e$ (0,0,z)
Lattice parameters		
a	3.848(1)	3.912(1)
c	13.953(3)	13.937(7)
z(I)	0.3660(2)	0.3641(2)
Temperature factor B	0.1(2)	1.1(2)
Assymmetry correction P	0.60(2)	−0.9(1)
half width[a]		
U	1.1(4)	0.7(2)
V	−0.4(1)	−0.4(1)
W	0.10(1)	0.12(2)
Pearson VII exponent m[b,c]	1.45(2)	1.29(3)
R/R_w[d]	7.7/5.7	10.8/8.2
R_{Bragg}[d]	4.6	9.7

[a]$H_w^2 = U \cdot \tan^2\Theta + V \cdot \tan\Theta + W$.

[b]Peaks below a chosen 2Θ angle are "corrected" for asymmetry by $1-P \cdot$ sign $(2\Theta_i - 2\Theta_k) \cdot (2\Theta_i - 2\Theta_k)^2/\tan\Theta_k$.

[c]Pearson VII profile function based on $R = 1/[1 + (2\Theta_i - 2\Theta_k)/H_w^2]^m$.

[d]$R = \dfrac{\Sigma \mid Y_o - Y_c \mid}{\Sigma \mid Y_o \mid}$; $R_w = \left(\dfrac{\Sigma (Y_o - Y_c)^2 \cdot w}{\Sigma Y_o^2 \cdot w}\right)^{1/2}$; $R_{Bragg} = \dfrac{\Sigma \mid I_o - I_c \mid}{\Sigma I_o}$.

band. A "spill over" from localized states into this band is energetically favorable and will lead to the observed metallic conduction.

Structural Data of the High-Pressure Phases

Table I gives the conditions and the results of a Rietveld refinement of powder data taken at ambient conditions for quenched NdI_2-II and for LaI_2 which crystallizes in the same structure at normal pressure. The Nd atoms are coordinated by eight I atoms in a cube-like arrangement at a distance of 3.302 Å. Within the plane of cations each Nd has four homonuclear contacts at 3.848 Å. Within a cube of anions arround Nd, the I–I distances along c are 3.739 Å and those in the (001) plane are 3.848 Å. Figure 1 shows how layers of face-sharing cubes centered by Nd atoms are stacked in a staggered

manner along c. The distances between iodide atoms in different double layers are much longer (4.299 Å). They compare well with the usual van der Waals contacts between iodide anions. The short I–I distances within an I–Nd–I sandwich imply a considerable change in bonding type in this phase as compared with the modification stable at ambient pressures. The same holds for the very short Nd–I distances, and this may well indicate a change in oxidation state of the Nd cations. The anisotropic metallic conductivity of these compounds has been explained earlier as a delocalization of a valence electron in a d-type band and formulas such as $Nd^{3+}(e^-)I_2$ have been given (1, 2).

Compressibilities in the Polymorphic Phases

Since the high-pressure phases can be retained as a metastable form at lower tempera-
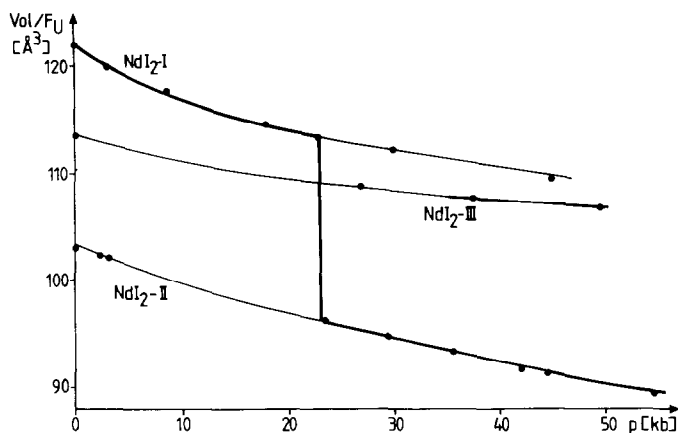
FIG. 4. Volume per formula unit vs pressure.

tures, their compressibilities could be measured beginning from ambient pressures in comparison with that of NdI₂-I. The compressibilities are illustrated in Fig. 4, where the change of volume per formula unit vs pressure is depicted. Individual lattice constants for the three phases at different pressures are given in Table II. This presentation

TABLE II

CHANGE OF LATTICE CONSTANTS WITH PRESSURE

| Compound	Pressure (GPa)	$a(\text{Å})$	$c(\text{Å})$	$V(\text{Å}^3)$
NdI₂-I				
	~0	12.573	7.658	1210.6
	0.31	12.540	7.620	1198
	0.83	12.480	7.550	1176
	1.8	12.397	7.471	1148
	3.0	12.322	7.385	1121
	4.5	12.240	7.310	1095
NdI₂-II				
	~0	3.844	13.94	206.0
	0.24	3.839	13.86	204.3
	0.31	3.836	13.83	203.5
	2.36	3.796	13.31	191.8
	2.95	3.790	13.19	189.5
	3.58	3.779	13.09	186.9
	4.39	3.763	12.95	183.4
	4.66	3.766	12.88	182.7
	5.65	3.745	12.73	178.5
NdI₂-III				
	~0	7.688		454.4
	2.69	7.578		435.2
	3.76	7.550		430.4
	4.97	7.527		426.4
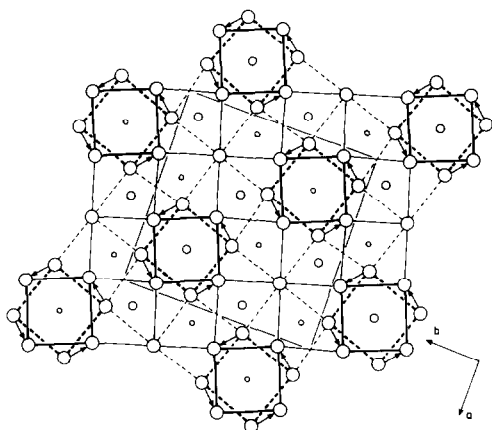
FIG. 5. View along [001] into an SrBr$_2$-type arrangement (arrows indicate the first steps of the movement of atoms during the transformation to the high-pressure phase.)

clearly reveals that the phase NdI$_2$-III is an intermediate between the other two. The volume reduction is only about 25% of the total change on going to the high-pressure phase.

The pressure dependence of the volumes of the thermodynamically stable phases can be fitted to a Murnaghan-type equation,

$$p = \frac{B_0}{B_0'} \left[\left(\frac{V_0}{V} \right)^{B_0'} - 1 \right],$$

giving the parameters B_0 25.3(4) and 30.0(10), or B_0, = 10.5(3) and 3.9(5), for NdI$_2$-I and NdI$_2$-II, respectively.

A Model for the Mechanism of Transformation

Comparing the structure of the high-pressure phase with the SrBr$_2$-type arrangement stable at ambient conditions a pathway for the transition can be conjectured. The SrBr$_2$ structure is basically an arrangement of two types of quadratic antiprisms in the manner of a cubic face-centered packing. In a view along [001], Fig. 5 shows the typical pattern of four more distorted antiprisms around an

almost ideal one to give a staggered stacking of planes with a chessboard-like structure. In a first step these antiprisms can be transformed to cube-like coordination polyhedra by an antisymmetric rotation of their base and top plane (arrows in Fig. 5). The arrangement of these cubes is topologically equivalent with that in the fluorite structure. In a subsequent step all cations within one layer parallel (001) must move out into the empty cubes of the adjacent layers, half of them moving upward along [001] the other half downward. This step needs a higher activation energy, and it is not surprising that we find the intermediate CaF$_2$ structure in the phase NdI$_2$-III, where the cation diffusion has not yet taken place. The cohesion of the structure in the empty double layers of anions, which are formed when the cations move out of every second plane, is enhanced by a subsequent shear along 1/2 $(a + b)$ which brings anions into a second coordination sphere of the cations giving an 8 + 2 coordination for every Nd atom.

In this Ti$_2$Cu-type arrangement the number of unoccupied voids has decreased considerably. According to the pressure coordination rule, the effective coordination number has increased. Since the stoichiometry has not changed, this is achieved by a higher degree of face and edge sharing of the coordination polyhedra, and this brings the close Nd–Nd contacts which are responsible for the mechanisms of metallic conduction.

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