Relation of Equilibrium Phase-Transition Pressure to Ionic Radii*

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Pressure–temperature equilibria curves for a series of some 20 rare-earth arsenates and rare-earth vanadates which undergo the reconstructive transition zircon ($ZrSiO_4$) ⇆ scheelite ($CaWO_4$) type structure in the region 10 000–60 000 atm were obtained. From these curves, a set of data were extracted representing (with a fair approximation to corresponding states) the change of equilibrium pressure for a transition as a function of the radius of the rare-earth ion. The result is a V-shaped curve for both vanadates and arsenates showing a minimum transformation pressure near Dy^{3+} or Ho^{3+}. An interesting even–odd effect is noted.

I. INTRODUCTION

THE only means available at present to predict if a phase change may be expected under high pressure are purely empirical. Prediction relies essentially on a correlation of the large number of isoformular phases (e.g., ABX_3, ABX_4, A_2BX_4 families) with the properties of the ions, chiefly their radii. It is not difficult, where such data are available, to indicate in what direction (i.e., to what structure) pressure or temperature cause a change of phase. Such prediction is sometimes unreliable because unexpected new phases appear.[1] Even if it is reliable, however, there is no indication of the magnitude of the pressure (or temperature) which could reasonably be expected to effect the transformation. Thus BPO_4 of cristobalite structure exists at atmospheric pressure and was found to undergo a transition to the quartz structure at about 45 000 atm at 500°C. The question to be answered is, at approximately what pressure does $BAsO_4$ show transition between the same two structures or, at least, is the required pressure higher or lower than for BPO_4? One difficulty in obtaining such data is clear; there are only a few ions with widely spaced radii and at most two or three analogous transitions may be found. The only solution to the latter problem is to work with the 4*f* series of rare earths. It is than necessary to find a family of compounds showing reconstructive "quenchable" transformation. The authors found[2] that the majority of the rare-earth vanadates and arsenates undergo the transformation zircon ($ZrSiO_4$) ⇆ scheelite ($CaWO_4$)-type structure at high pressure, and these compounds were used in the present study.

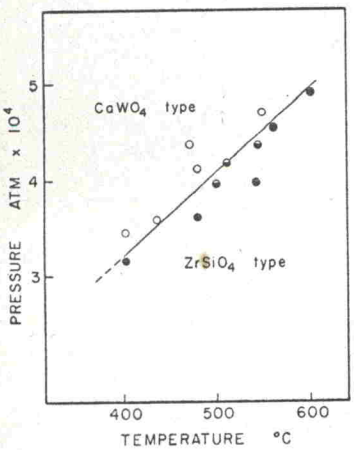

FIG. 1. Univariant pressure–temperature curve for the transition zircon-type ⇄ scheelite-type structure in $DyVO_4$.

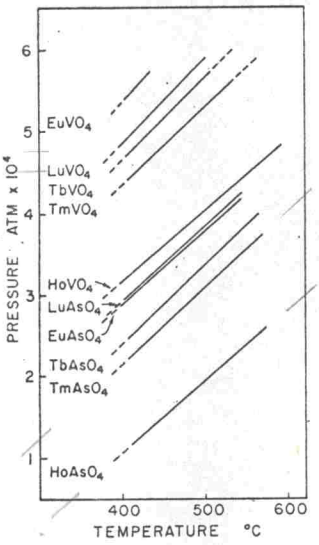

FIG. 2. Univariant pressure–temperature curves for the transition zircon-type ⇄ scheelite-type structure in the rare-earth vanadates and arsenates. Rare-earth atoms with odd atomic numbers.

II. EXPERIMENTAL PROCEDURE

The rare-earth orthovanadates were synthesized by solid-state reaction from mixtures of 99.9% purity rare-earth oxides V_2O_5, by heating at 950C° for a period of 8 h. The rare-earth arsenates were prepared by precipitation from boiling water solutions of rare-earth nitrates and Na_2HAsO_4. Well-crystallized arsenates were obtained after heating precipitates at 650°–700°C for a period of 7 days.

The high-pressure experiments were performed with externally heated uniaxial devices, using pistons of

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[1] F. Dachille and R. Roy, Z. Krist. 111, 451 (1950).

[2] V. Stubican and R. Roy, *Proc. XVIIIth Int. Congr. Pure and Appl. Chem., Montreal, Canada, 1961*, p. 72 (abstract); Z. Krist. (to be publisded).

cemented carbides and hardenable steel. The full description of the high-pressure apparatus used in our study can be found elsewhere.[1] The samples were pelleted into nickel rings (0.010 in. thick), sandwiched between two Pt–Rh sheets, and placed between two pistons on which high pressure was applied. After 24–48 h the specimens were quenched to the room temperature with a stream of cold air and the pressure was released. Temperature and pressure were automatically controlled. The structure of the specimen was determined by the x-ray diffraction method. A word needs to be said regarding the accuracy and precision of the data. The temperature was accurate to ±5°C, and the pressure to ±5% from 25 000–50 000 atm and ±7% from 10 000–25 000 atm. The univariant pressure–temperature curves were generated from about 15–20 points.

III. RESULTS AND DISCUSSION

In Fig. 1 the univariant pressure–temperature line for the transition zircon ⇄ scheelite-type structure for

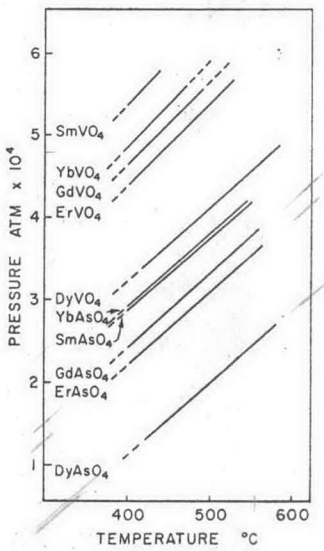

FIG. 3. Univariant pressure–temperature curves for the transition zircon-type ⇄ scheelite-type structure in the rare-earth vanadates and arsenates. Rare-earth atoms with even atomic numbers.

$DyVO_4$ is shown. Black circles indicate the specimens with zircon-type structure, open circles the specimens with scheelite-type structure, and black and white circles the specimens containing mixtures of both forms. Figure 1 shows that the univariant p–t line could be easily drawn in this case, because no reverse change occurs during quenching. In Figs. 2 and 3 are given the univariant p–t curves for four familes of the rare-earth vanadates and arsenates. The strong influence of the specific rare-earth ions on the position of the equilibrium is clearly demonstrated. Furthermore, comparison of the univariant p–t curves for the rare-earth vanadates with p–t curves for the rare-earth arsenates, make it evident that the influence of the second ions in the structure (V^{5+}, As^{5+}) is very pronounced.

From Figs. 2 and 3 a set of data can be extracted

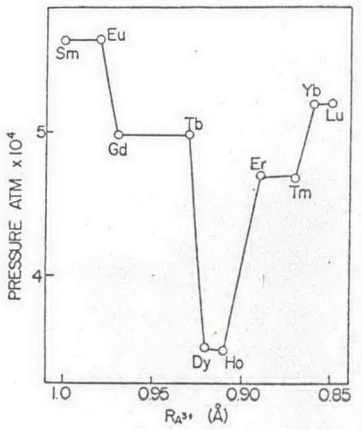

FIG. 4. Relationship between the equilibrium transition pressures at 430°C and the ionic radii of the rare-earth ions. Transformation zircon-type ⇄ scheelite (high pressure form) structure in the rare-earth vanadates.

showing the relationship between the ionic radii of the rare-earth ions and the equilibrium transformation pressure, e.g., at 430°C as is shown in Figs. 4 and 5. The same type of curves could be obtained at any other temperature between 380°–600°C due to the fact that the p–t lines are almost parallel.

Both curves (Figs. 4 and 5) show a minimum near Dy^{3+} or Ho^{3+}. Furthermore, two neighboring rare-earth ions, with odd and even atomic numbers, respectively, show approximately the same transformation pressure in spite of the difference in the size of ions.

The results show that the ionic size is not the only factor which determines the minimum transition pressure, at least not when the rare-earth ions are involved.

The only other similar data in the literature, although obtained by different means (volume decrement measurement), are those on the alkali halides obtained by Bridgman.[3] Assuming that all the changes reported correspond to the NaCl ⇆ CsCl-type structure transition, because experimental high-pressure x-ray data are available for only a few, we can compare the transition pressures at about 300°K for several alkali halides (Table I). Although few data are available, they follow the trend of higher pressure with smaller cation or anion. The difference between this case and that of the

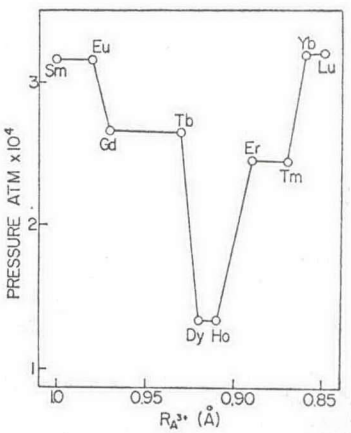

FIG. 5. Relationship between the equilibrium transition pressures at 430°C and the ionic radii of the rare-earth ions. Transformation zircon-type ⇄ scheelite-type structure in the rare-earth arsenates.

[3] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. 76, 1 (1945).

TABLE I. Transition pressures for alkali halides. (data extracted from the work of Bridgman.)[a]

	Pressure kg/cm²		Pressure kg/cm²		Pressure kg/cm²
KCl	20 060	KBr	18 400	KI	18 200
RbCl	5000	RbBr	4600	RbI	4050

[a] See Ref. 3.

rare-earth vanadates or arsenates is of course great. The zircon-to-scheelite structure transition involves no major coordination change, but the density increase (approximately 11%) results from a much more efficient packing and the elimination of a structural hole in a zircon-type structure.

Furthermore, the influence of the magnetic spin coupling at high pressure with rare-earth ions is possible. This may account for the even–odd similarity. It is known that the $4f$ electrons of rare-earth ions are responsible for the paramagnetism. The curve showing the relationship between effective numbers of Bohr magneton and atomic numbers of the rare earths[4] has a pronounced maximum at Dy^{3+} and Ho^{3+} where the present curves (Figs. 4, 5) show a minimum.

ACKNOWLEDGMENT

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Fluctuations in Hot Tungsten Filaments*

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The high-frequency spectral noise voltage appearing across a metallic conductor electrically heated to high temperatures is experimentally found to be in agreement with the Nyquist theorem even though the conductor is far from thermodynamic equilibrium. Furthermore, because of the thermal origin of the nonlinearities in the current–voltage characteristic the proper value of resistance to use in the Nyquist expression corresponds to the voltage/current ratio, rather than the differential resistance at the operating point. At frequencies below that corresponding to the thermal time constant of the conductor, an additional noise voltage caused by temperature fluctuations is detected. The observed magnitude and spectrum of this noise voltage is in very good agreement with a simple calculation of temperature fluctuations due to heat conduction.

I. INTRODUCTION

IT is well established that the random electrical fluctuations at the terminals of a conductor of resistance R are given in terms of spectral noise voltage by the Nyquist theorem[1]:

$$\langle \Delta v^2 \rangle = 4kTR, \tag{1}$$

where k is Boltzman's constant and T is the absolute temperature. The Nyquist expression is valid only if the conductor is in thermodynamic equilibrium with its surroundings. Since a comparable expression has not been developed for the nonequilibrium case, Eq. (1) is commonly used to define a noise temperature in such experimental studies as hot electrons in semiconductors[2] or electrons in gaseous plasmas,[3] with the expectation that the noise temperature may be a good measure of the true temperature of the electron gas.

A preliminary experimental confirmation of the validity of the Nyquist expression in a simple non-equilibrium situation has been obtained in a study of the noise in metal bolometers[4] at relatively small departures from equilibrium. The present measurements extend these results to considerably higher temperatures when the conductor is far from equilibrium and is losing heat by radiation. The spectral noise voltage appearing across a metallic conductor heated to high temperatures by dc flow is investigated. This experiment was chosen because it is relatively easy to attain high sample temperatures which can be determined independently by straightforward optical pyrometer techniques. Furthermore, the influence of other possible noise sources, such as current noise, is reduced by studying metallic conductors. A particular item of interest is the proper value of resistance to be used in the Nyquist expression when the specimen has a nonlinear current–voltage characteristic. It is not clear *a priori* whether the apparent resistance, e.g., the voltage/current ratio

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[4] K. Scheidbauer, Z. Angew. Phys. 13, 380 (1961).