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The Stability Region of  $\text{CrO}_2$  at High Temperature and  
High Pressure and the Synthesis of Spinel-type Oxides Containing  $\text{Cr}^{4+}$   
by Osamu FUKUNAGA, Akira SAWAOKA, Shinroku SAITO  
(Discussion on the Artificial Minerals at Osaka in 1965)

Abstract

1. Stability region of  $\text{CrO}_2$

$\text{CrO}_2$  has been synthesized under high oxygen pressure by previous investigators. The authors found that  $\text{CrO}_2$  was stable in the higher temperature range under solid pressure. The starting material of the runs was underfired  $\text{CrO}_3$  whose composition was  $\text{CrO}_{2.5}$ . The apparatus used was a piston-cylinder type high pressure apparatus. The boundary curve between  $\text{CrO}_2$  and  $\text{Cr}_2\text{O}_3$  was given by the expression,

$$P(\text{kb}) = 7.4 + 0.019T(^{\circ}\text{C})$$

2. Synthesis of  $\text{Me}_2\text{CrO}_4$

If spinels like  $\text{Me}_2\text{CrO}_4$  ( $\text{Me} = \text{Mg}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}$ ) are satisfactorily synthesized, it is expected that  $\text{Cr}^{4+}$  ion may be contained in crystal. The results, however, were contradictory. With magnetic measurement, the curie point of  $\text{Co}_2\text{CrO}_4$  was in accordance with that of  $\text{CoCr}_2\text{O}_4$ . The lattice constant of the former was 8.24Å, while the latter 8.33 to 8.35Å.

## The Effect of Pressure on the Transition of $ZrO_2$

by Osamu FUKUNAGA, Shigeru MINOMURA, Shinroku SAITO  
The 3rd Discussion on the Basic Science of Ceramics  
at Kyoto in 1965

### Abstract

The effect of pressure on the monoclinic-tetragonal reversible transition of  $ZrO_2$  was investigated. The pressure dependency of the above transition was estimated to be  $dT_c/dP = -3.02 \times 10^{-2}$  deg.bar<sup>-1</sup> from the thermodynamic data of  $ZrO_2$  by Whitney. As the experimental result has not been obtained yet, the experiment of the pressure effect on this transition was tried, to compare it with the calculated value.

A Kennedy type piston-cylinder high pressure apparatus was used and the transition points were detected by the electrical resistance measurement of  $ZrO_2$  under high temperatures and high pressures.

The measurements were carried out in the temperature and pressure ranges up to 1300°C and 30 kb, respectively.

One sample of  $ZrO_2$  used in the present experiment is the  $ZrO_2$  powder obtained by Monsanto Chemical Co. Using the above sample, the transition point and the molar volume change were measured by High temperature X-ray diffraction at the atmospheric pressure. The monoclinic-tetragonal transition point  $T_c^{M \rightarrow T}$  was 1140°C and the molar volume change  $\Delta V^{M \rightarrow T}$  was  $-0.95 \text{ cm}^3/\text{mol}$ . As the entropy change,  $S^{M \rightarrow T}$ , the value by Coughlin and King was used, which is  $S^{M \rightarrow T} = 0.96 \text{ cal/mol.deg}$ . Using the Clausius-Clapeyron equation, the pressure effect on the transition was calculated to be  $-1.2 \times 10^{-2}$  deg.bar. On the other hand, the pressure dependency of the transition point obtained by the experiment was  $-1.6 \times 10^{-2}$  deg.bar.

## The Effect of Pressure on the Electro-Magnetic Property of NiO

by Osamu FUKUNAGA, Shinroku SAITO, Shigeru MINOMURA

The 3rd Discussion on the Basic Science of Ceramics  
at Kyoto in 1965

### Abstract

Nickel and cobalt oxides, whose 3d orbitals are not filled in the free electron states, are considered to have metallic conductivities from the band theory. The fact, however, is that these stoichiometric compounds are insulators. Non-stoichiometric NiO and Li-doped NiO ( $\text{Li}_x\text{Ni}_{1-x}\text{O}$ ) have the resistivities of the order of several ohm.cm. almost equal to that of VO, TiO etc., which show metallic conduction, but the temperature coefficient of the resistivities of the former are still negative and semiconductors in this sense.

In the present experiment, the electric conductivities of NiO and Li-doped NiO were measured at very high pressure and it was tried to explain the high pressure effect on the conductivity from the point of view of the hopping model. A Kennedy-type of a high pressure piston-cylinder apparatus and a simple squeezer with Bridgman-type anvils were used in the present experiment.

One example of the experimental results in  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  in case of  $x = 0.1$  is described below. As shown in Figs. 1, 2, 3, the electric conductivity decreased with increasing pressure at constant temperature. The pressure coefficient of the activation energy of the electric conductivity of  $\text{Li}_{0.1}\text{Ni}_{0.9}\text{O}$  was estimated to be  $\Delta V_{\text{act.}} = (\partial q / \partial p)T = -1.02 \sim 1.94 \times 10^{-6}$  eV/bar and  $(\partial q / \partial p)T < 0$ .

This means that at the time of hopping of a positive hole, the distance between  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  seems to be shorter than the relaxation of lattice, which makes it difficult to explain the mechanism of the electric conduction from the hopping model.

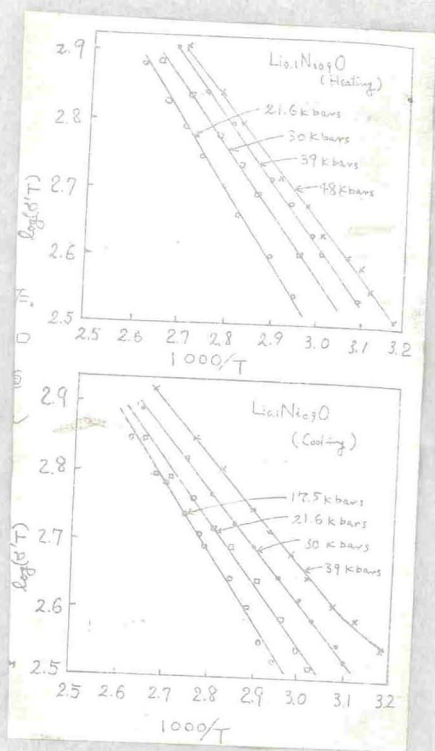


Fig. 1

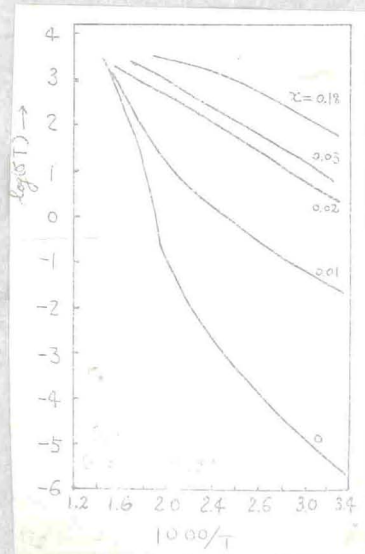


Fig. 2 Li<sub>x</sub>Ni<sub>1-x</sub>O at atmospheric pressure

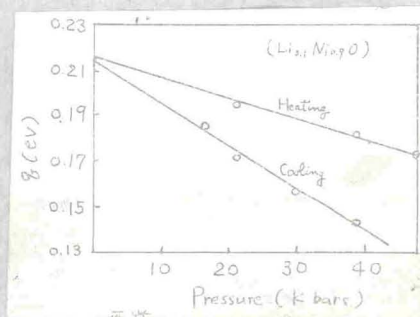


Fig. 3 Pressure change of activation energy of electric conduction

High Pressure Synthesis of Perovskite-type  
Oxide Complex Containing Pb<sup>2+</sup>

by Osamu FUKUNAGA, Takehiro NAKAGAWA,  
Shoichiro NOMURA, Shinroku SAITO

(The Japan Society of Physics at Okayama in 1965)

Abstract

It is difficult to synthesize some perovskite structure-type oxide complex  $A(B_xB'_{1-x})O_3$  containing Pb<sup>2+</sup> at A-site and paramagnetic ions Ni<sup>2+</sup>, Co<sup>2+</sup>, Co<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, etc. in a part of B-site at atmospheric pressure because PbO and Bi<sub>2</sub>O<sub>3</sub> easily sublime and have low melting temperatures. The melting temperatures, however, increase with increasing pressure. Satisfactory results were expected in the synthesis of these compounds at high temperatures and high pressures. A piston-cylinder type high temperature-high pressure apparatus was used in the range to 45 kb., 1700°C. Table 1 shows the experimental results and Pb(NiW)<sub>1/2</sub>O<sub>3</sub>, Pb(Co<sub>2/3</sub>W<sub>1/2</sub>)O<sub>3</sub>, etc. were synthesized satisfactorily.

Table 1

	Temp. (°C)	Pres. (kb)	Duration (hr)	Starting Material	Note
Pb(CoW) <sub>1/2</sub> O <sub>3</sub>	850	35	1	PbO, CoCO <sub>3</sub> , H <sub>2</sub> WO <sub>4</sub>	Perovskite $a=8.030\text{\AA}$
Pb(NiW) <sub>1/2</sub> O <sub>3</sub>	850	35	1	PbO, NiO, H <sub>2</sub> WO <sub>4</sub>	" $a=7.977\text{\AA}$
"	1200	36	1	"	" + (?)
"	800	30	2.5	"	"
Pb(Co <sub>2/3</sub> W <sub>1/3</sub> )O <sub>3</sub>	850	30	10min.	PbO, CoCO <sub>3</sub> , H <sub>2</sub> WO <sub>4</sub>	" $a=8.021\text{\AA}$
Pb(FeW) <sub>1/2</sub> O <sub>3</sub>	850	30	1	PbO, FeO, H <sub>2</sub> WO <sub>4</sub>	" + pyrochlore
Pb(CoMo) <sub>1/2</sub> O <sub>3</sub>	850	30	1	PbO, CoO, MoO <sub>3</sub>	" - PbMoO <sub>4</sub>

Detecting Methods of Solid-Liquid and Solid-Solid Phase Transitions  
in Inorganic Compounds at High Temperatures and Pressures

by Shinroku SAITO, Yoshiharu OZAKI, Shinobu YAMAOKA, Osamu FUKUNAGA

The 4th Discussion on the Basic Science of Ceramics  
at Nagoya in 1966

Abstract

Many investigations about solid-liquid and solid-solid phase transitions have been done under high pressures and high temperatures, and still it is important. The discovery of new phases under high pressures and temperatures about silicate minerals, seems to have been worked out. However, there still remains a lot of questions on the stable regions. The data of the P-T diagram about solid-liquid and solid-solid phase transitions under atmospheric pressure are poor. In our laboratory we are collecting data of solid-solid and solid-liquid phase transitions using a quenching method, a differential thermal analysis (DTA) method and variations of the electrical resistance, etc. Especially in present paper dynamic methods (the DTA, the electrical resistance measurement) are shown and some results obtained by using these methods are discussed.

1. Apparatus

Pressures were generated by a piston-cylinder apparatus. After a sample was set in a high pressure cylinder vertically supported by two separate 150-ton rams, it was pressed by a 600-ton rams. The apparatus was calibrated by Bi(1)-Bi(2) 25.4 kb, Bi(2)-Bi(3) 27.0 kb, and Tl(2)-Tl(3) 36.7 kb.

2. Experimental Procedure

(a) Electrical resistance measurement: The principle of this method is an abrupt change of electrical resistance after solid-solid phase transitions. A sample assembly is shown in Fig. 1. In this method a thermal electrical motive force is generated by a temperature difference between the sample ends.

(b) DTA method: The DTA method was developed for the investigation of the melting curves of the pure metals at high temperatures and pressures by Kennedy, Newton, and Jayaraman. The DTA method is

especially useful for the investigation of the melting curves, but it is difficult to use over 1300 °C as there is no suitable sample container. In this respect this method wants more development.

### 3. Experimental Results

(a) Monoclinic-Tetragonal transition of  $ZrO_2$ : As Fig. 2 shows, transition was detected from the abrupt change point of the curve plotted  $\log R$  (resistance ohm) vs.  $1000/T$  (°K). In this experiment a volume change  $\Delta V = 0.52 \pm 0.07$  cc/mole using by a high temperature x-ray diffraction at the atmospheric pressure,  $\Delta H = 1420 \pm 3$  cal/mole (by Coughlin-King) and a transition temperature  $T_c = 1383 \pm 10$  °K at the atmospheric pressure. So  $dT_c/dP = -1.20 \pm (0.16) \times 10^{-2}$  deg/bar was decided by the Clapeyron equation. This value was reasonable. The pressure dependence of the monoclinic-tetragonal transition of  $ZrO_2$  is shown in Fig. 3.

(b)  $\alpha$ - $\beta$  transition of Quartz: This transition has been investigated up to 10 kb. by Yoder. We investigated up to 30 kb. by the DTA method and decided the triple point of  $\alpha$   $SiO_2$  -  $\beta$   $SiO_2$  - Coesite.  $dT_c/dP = 2.87 \times 10^2$  deg/bar was consisted with the Yoder's value. But this curve was not linear, but it was concave toward the pressure axis. This result is shown in Fig. 4.

(c) Melting curves of AgCl: Melting curves of AgCl, AgBr,  $AgNO_3$ , NaCl, KCl, etc. were determined up to 40 kb. using the DTA method. These results were summarized by the Simon's equation. For example the Simon's equation of AgCl is shown in  $P(kb) = 13.5 [(T/728)^{4.3} - 1]$ , Fig. 5 shows the melting curve of AgCl and DTA signals. Data of other materials are to be shown in another paper.



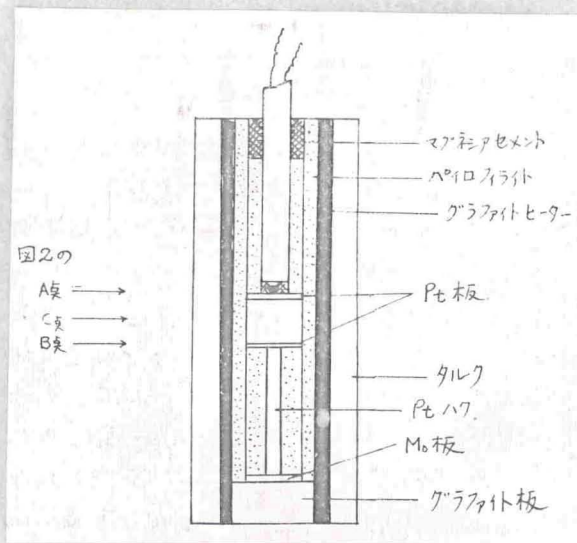


Fig. 1 Sample Assembly

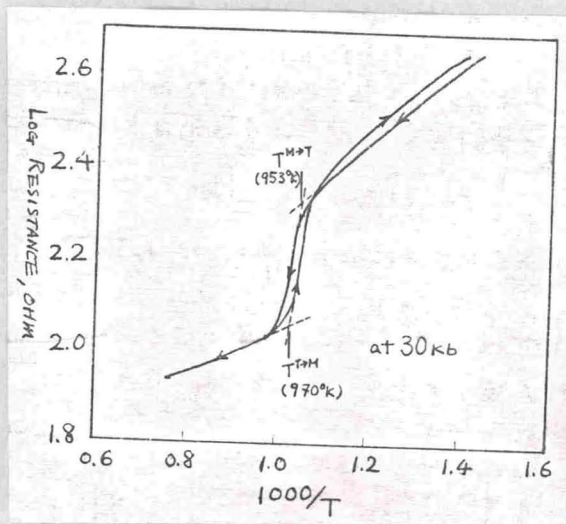


Fig. 2 Log Resistance of  $ZrO_2$  vs.  $1000/T$  at 30 kb.

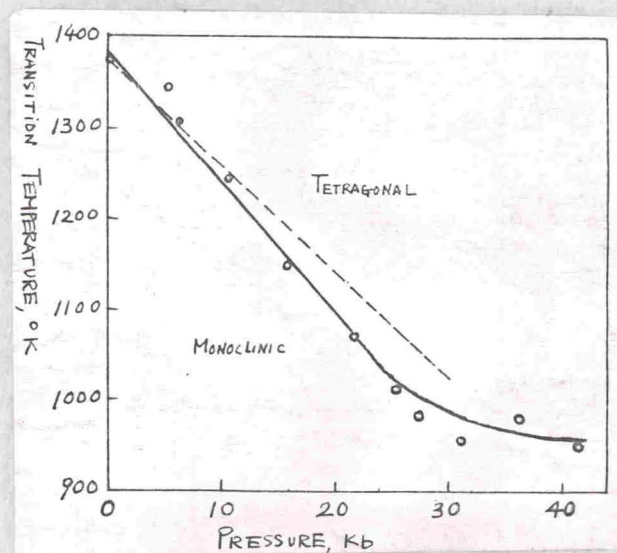


Fig. 3 Pressure dependency of Monoclinic  $\rightarrow$  Tetragonal transition of  $ZrO_2$  (solid line..observed) (dotted line..calculated)

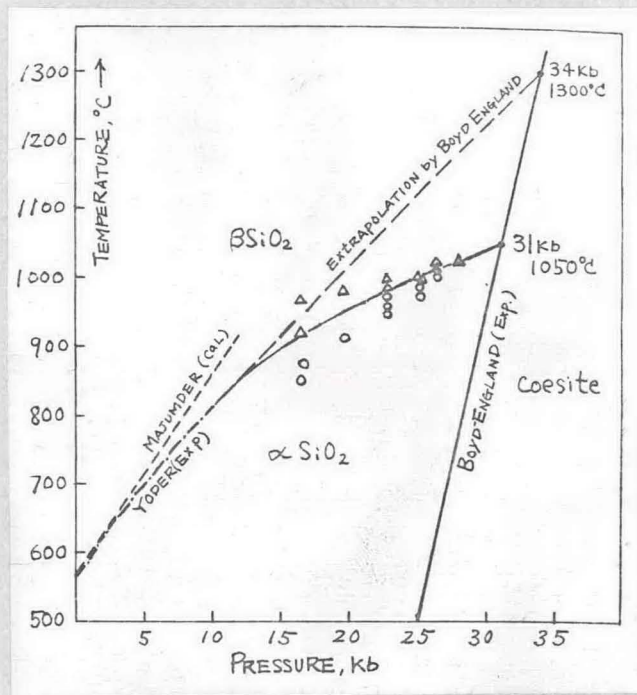


Fig. 4 Transition curve of  $\alpha$ - $\beta$  Quartz

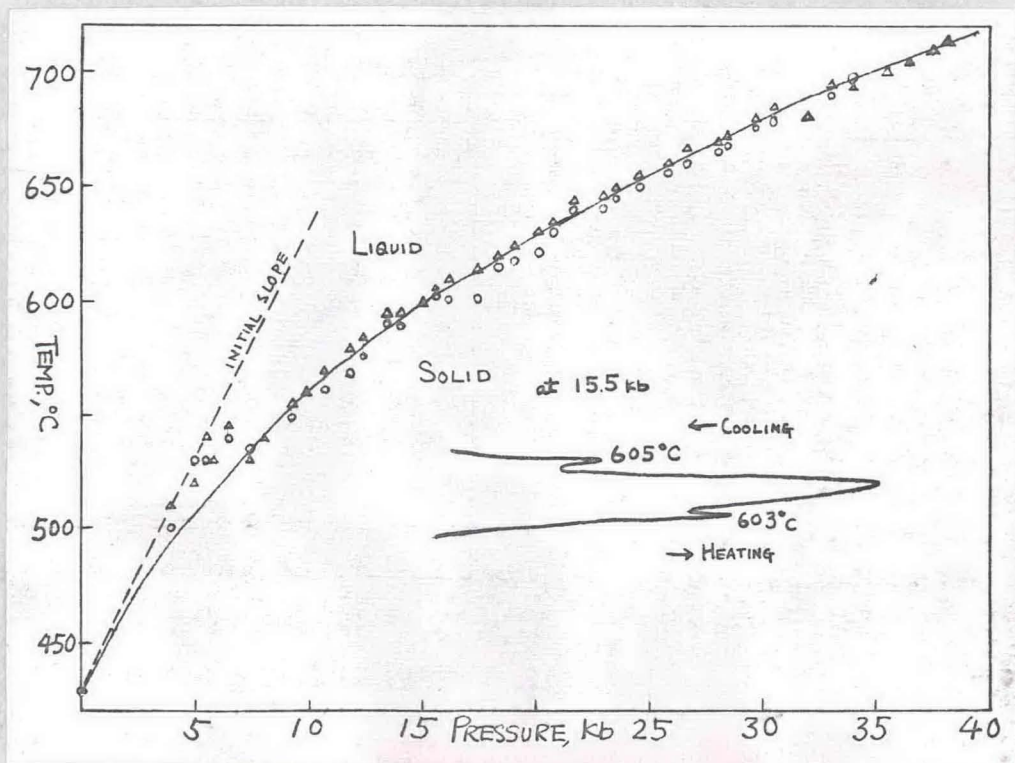


Fig. 5 Melting curves of AgCl  
(O..heating  $\Delta$ ..cooling)

## The Electrical Conductivity of NiO-System under High Pressure(II)

by Osamu FUKUNAGA, Shinroku SAITO, Shigeru MINOMURA

The 4th Discussion on the Basic Science of Ceramics  
at Nagoya in 1966

### Abstract

In the present experiment, these were investigated. (1) The variation of the electric resistance and the activation energy of conductivity of Li-doped NiO with Li concentration at high pressure. (2) The Seebeck coefficient in the temperature range from room temperature to 700 °C. (3) The pressure dependency of the Neel point of NiO were investigated. The Seebeck coefficient was obtained by measuring temperature difference and potential drop fixing two couples of thermocouple on the both ends of a sample under high pressure generated by a piston-cylinder type high pressure apparatus. The electric coefficient was measured by Bridgman-type anvils with radii of 5.64 mm and 10 mm. Temperature dependency of the resistance of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  is given by the following expressions,

$$T/R = A_1 \exp(-q_1/kT) \quad \text{at } T > T^*$$

$$T/R = A_2 \exp(-q_2/kT) \quad \text{at } T < T^*$$

where  $T^*$  is nearly Neel temperature. In the range,  $x < 0.02$ ,  $q_1$   $q_2$ , and in the range  $x > 0.02$ ,  $q_1$   $q_2$ .

Fig. 1 shows the pressure variance of  $q_1$  and  $q_2$  of samples at  $x = 0.01$  and  $x = 0.1$ . If the result above 30 kb. was extrapolated to the atmospheric pressure, it agreed with the value obtained by the measurement using a single crystal. At the pressure less than 30 kb., however, pressure dependency of  $q$  was not linear.

Fig. 2 shows the result of the measurement of the temperature variance of Seebeck coefficient under the high pressure. As all of them had positive thermo-emf ( $\mu\text{V}.\text{deg}^{-1}$ ), they were considered to have positive hole conduction. According to Heikes,

$$\alpha = k/e(Q/2kT - \ln C_0/(1 - 2C))$$

where  $Q$  is trapping potential,  $C$  is hole concentration, and  $C_0$  is concentration of dopant. Therefore, plots of  $\alpha$  ( $\mu\text{V}.\text{deg}^{-1}$ ) vs.  $1000/T$  become linear.

Fig. 3 shows the plots of  $\alpha$  vs.  $1000/T$ . The pressure dependency of these Seebeck coefficient was positive and was contrary to the result by Young et al.

Fig. 4 shows the pressure dependency of Neel temperature  $T_N$  of non-Li-doped NiO (green NiO powder)  $dT_N/dP$  was nearly  $2.6 \times 10^{-3}$  deg.bar<sup>-1</sup> which was almost in accordance with the estimate by Janusz,  $dT_N/dP = 2.0 \times 10^{-3}$  deg.bar<sup>-1</sup>.

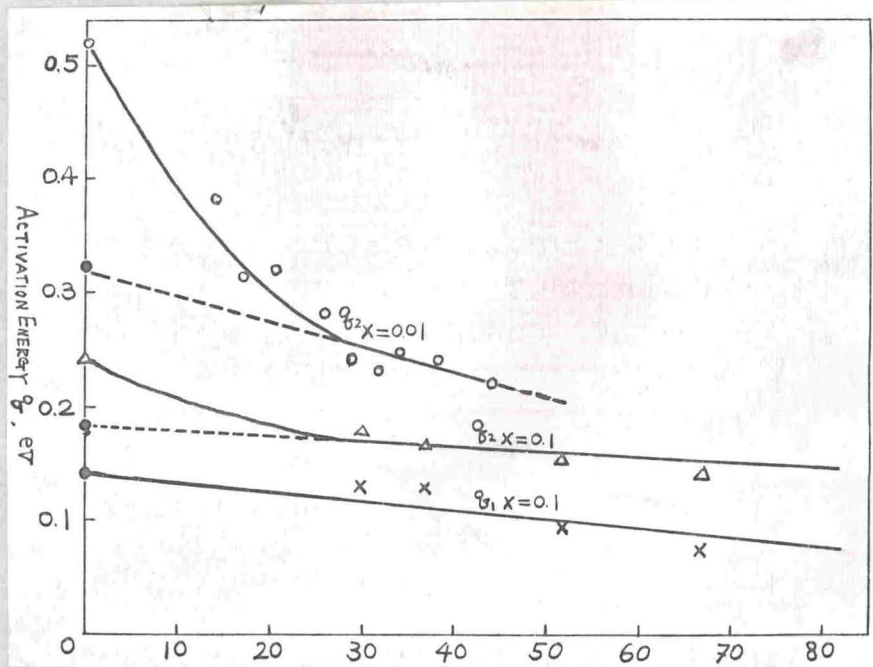


Fig. 1 Pressure change of Activation Energies  $q_1$ ,  $q_2$  at  $x=0.01$  and  $x = 0.1$  of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  by Koide

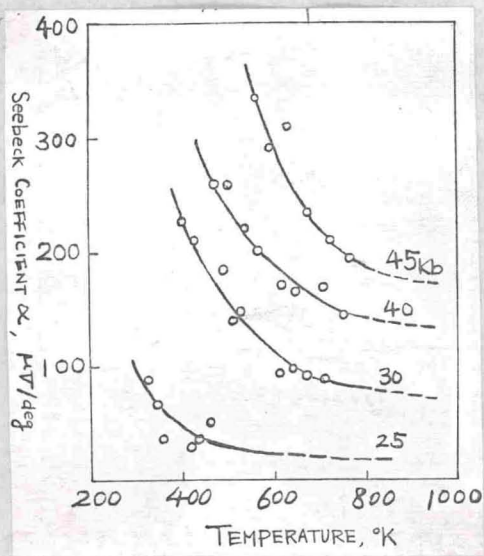


Fig. 2  $\alpha$ -T curves at  $x=0.1$

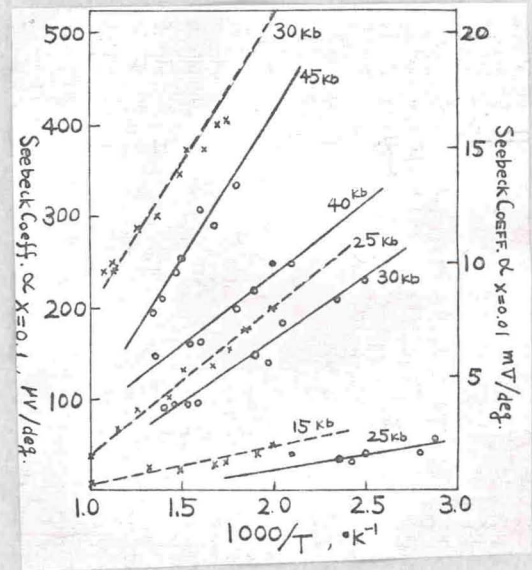


Fig. 3  $\alpha$  vs.  $1000/T$  at  $x=0.1$  (solid line) and  $x=0.01$  (dot. line)

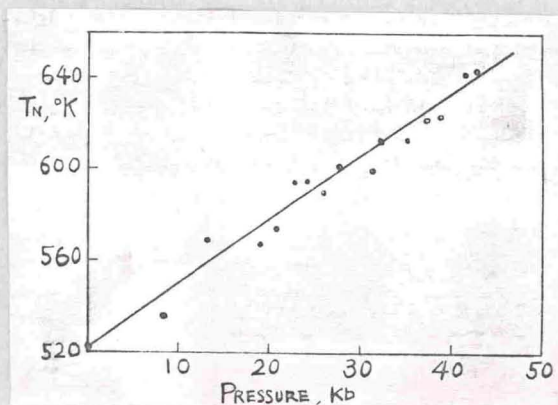


Fig. 4 Pressure Dependency of Néel Temp. ( $T_N$ ) of NiO

## Differential Thermal Analysis of $\text{KNO}_3$ under High Pressures

by Shinroku SAITO, Osamu FUKUNAGA, Shinobu YAMAOKA and Yoshiharu OZAKI

### Abstract

A phase diagram of  $\text{KNO}_3$  was determined up to the pressure and temperature of 45 kbar and  $600^\circ\text{C}$  by differential thermal analysis using a single-stage piston-cylinder type high pressure apparatus. This paper discusses in detail the modification of Kennedy's press for DTA study, pressure measurement in the sample cell and temperature measurement under high pressures. Three new polymorphs of  $\text{KNO}_3$ , phase V, phase VI and phase VII were detected by the DTA technique.

(1) Kennedy's press was modified to serve easy-controlling of press space by changing end-loading ram position. Several techniques for preventing the shortening of the lead wires were discussed.

(2) Pressure measurements in the cell of talc-AgCl were carried out using Bi and Tl foil with a electrical resistance change technique. The calibration curve for a 30 mm. long cell based on the measurement at room temperature was obtained as follows;

$$P = 0.97 L - 4.7 \text{ (kb.)}$$

(3) The change in emf of Chromel/Alumel thermocouple with pressure up to 31 kb. was laid within  $20^\circ\text{C}$  at  $600^\circ\text{C}$ .

(4) Phase diagram of  $\text{KNO}_3$  above 14 kb. was similar to those of  $\text{CsNO}_3$ ,  $\text{TlNO}_3$  and  $\text{RbNO}_3$ .

Phase Equilibrium in the System  $MgO-H_2O$  at High Temperatures  
and Very High Pressures up to  $1500^{\circ}C.$ , 50 kilobars

by Shinobu Yamaoka, Osamu Fukunaga, Shinroku Saito

Abstract:

The phase equilibrium in the system  $MgO-H_2O$  at high temperatures and very high pressures was investigated using a piston-cylinder type high pressure-high temperature apparatus. The pressure-temperature curve of brucite was given experimentally from 4 kb. to 25 kb. water pressures by the following expression,

$$\log P_{H_2O}(\text{kb}) = -3.18 \times 10^3/T (^{\circ}K) + 3.91$$

Brucite, however, did not decompose to periclase but melted congruently at water pressures greater than about 25 kb. The melting curve was measured by differential thermal analysis up to 50kb. and the pressure gradient of the melting temperature,  $dT_m/dP$  was approximately  $2.0^{\circ}C/kb.$

As the liquid phase was non-quenchable, X-ray powder diffraction pattern of the quenched sample from the liquid phase did not show the presence of glass but crystalline brucite, while this was clearly distinguished from the original brucite phase by microscopic observation, affirming the existence of the liquid phase.

Influence of Hydrostatic Pressure on the Mechanical  
Properties of Heat Treated Steel

by Shinroku SAITO, Norio KANETAKE, Toshimitsu TSUMURA

Abstract

The stress distribution of heat treated steel can be remarkably changed with the condition of heat treatment, while the similar phenomenon can be expected by pressure treatment, which means here in this paper to bring metals under isostatic high pressure environment after thermal preparations.

The purpose of this paper is to find the manner how the residual stress should be distributed in steel rod specimen after pressure treatment and concerns also to what mechanical properties should be brought as the results.

Two types of high pressure vessels were designed. The smaller one has the pressure chamber of  $35\phi \times 150 \text{ mm}^3$  and the larger one consists of two chambers of lower and higher pressures respectively. In other words, the inner shell of higher pressure is enclosed by the annular outer cylinder and has the volume of  $100\phi \times 200 \text{ mm}^3$  enough to set a certain heating device within. But the present paper is only limited to the pressure treatment at room temperature.

Change of residual stress distribution: Residual stress distribution is changed almost to the opposite sign. For example, in case of SCM 22 steel specimen (0.9 mm rod; 0.2 C, 1.1 Cr, 0.2 Mo), residual tensile stress of about 40 kg/mm takes place on the surface as oil-quenched, while this disappears after pressure treatment of 2000 kg/cm<sup>2</sup> and compressive stress of about 20 kg/mm<sup>2</sup> can be observed instead. In general, the stress distribution along principal axis of quenched steel rod is as following across the cross section; tensile stress at the central part, compressive stress at the middle annular part and tensile stress takes place again at the outer part, increasing larger towards the surface. But after pressure treatment this pattern is altered almost upside-down.



Change of specific volume: The initial specific volume of the same specimen upper mentioned is 0.12798 cm<sup>3</sup>/g as quenched. Increasing the amount of the applied pressure up to 2000 kg/cm<sup>2</sup>, a monotonous decrease of specific volume is observed up to 0.12789 kg/mm and the slope becomes extremely gentle after about 2000 kg/cm<sup>2</sup>.

Variation of surface hardness: The existence of compressive stress on the surface suggests that the surface hardness and mechanical strength may be increased. In a case of low carbon steel, experiments show that the surface hardness can be increased in every case of changing pressure levels as well as temperature levels of tempering, this is, 2000~6000 kg/mm as pressure level and 100~400°C as temperature level in addition to the level of as quenched. This inclination is held even in the cases of high speed steels and special steels.

Increase of tensile strength, reduction and elongation: These values are increased in nearly same fashion. The slopes before 2000 kg/cm<sup>2</sup> of applied pressure are steeper than the ones after 2000 kg/cm<sup>2</sup>. In a case of SCM 4 steel (0.4 C, 1.1 Cr, 0.2 Mo) the increment of elongation is observed as much as 20 %. Contradiction between simultaneous increases of hardness and plasticity seems to be contributed to the increment of dislocation generated in the event of changing of the stress distribution.

Effects on impact value: Impact values are also increased but gets remarkable effect by tempering temperature, having the maximum points at about 200°C, indifferent to pressure levels.

Increase of endurance limits: Fatigue test reveals that pressure treatment brings favourable effect on endurance limit.