The Use of Radioactive Fission Product Rare Gases for the Study of the Change in Crystal Structure

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In our previous paper(1), the possible correlation between released fission rare gas which was captured in a sample of hematite by its recoil energy and the crystal structure change was reported, and the use of radioactive fission product rare gas for the emanation method in place of radon was proposed. In our present work, the experiment was carried out more extensively using the high temperature X-ray diffraction method to confirm the correlation. The usefullness of this emanation method using radioactive fission rare gas in place of radon for the studies in the field of physical chemistry is also discussed.

Experimental

Usable Nuclides in Fission Product Rare Gases for the Emanation Method.—A major fraction of Uranium-235 thermal fission products consist of gaseous materials and the sum of independent and primary cumulative yields of all gaseous fission products, including iodine, bromine, xenon and krypton, amount to 52.3%. Of this value 55.3%, or a yield of 28.9%, is attributed to xenon and krypton.

Referring to a table of isotopes(2), krypton-85m, xenon-135 and xenon-133 have considerably long half-lives and large fission yields. To investigate the interference of the precursor and the radioactivity of the other nuclides, the changes of the radioactivity of the krypton-85m, xenon-135 and xenon-133 after two hours' irradiation with time are measured and these changes are plotted in Fig. 1. In these experiments, a closed polyethylene sheet containing 20 mg. of uranium dioxide was irradiated

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(1) S. Yajima, S. Ichiba, Y. Kamemoto and K. Shiba, This Bulletin, 33, 426 (1960).

(2) e. g., D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.*, 30, 585 (1958).

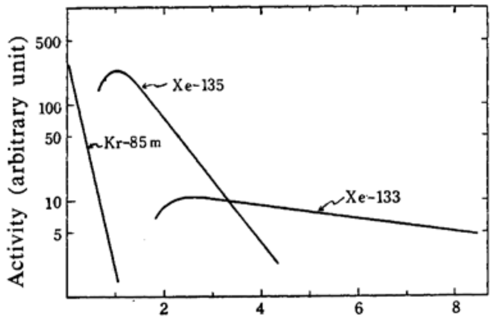

Fig. 1. Change of the radioactivities of the fission product krypton and xenon with time after two hour irradiation.

by thermal neutrons (flux, ~5×10^{11} n/cm^2 sec.) for two hours. The sample is placed in a small flask after each cooling period and the sheet is broken, and the uranium dioxide is dissolved in concentrated nitric acid. Helium is made to flow through the flask, a trap is cooled by dry ice (for iodine) and a charcoal trap is cooled by liquid nitrogen (for xenon and krypton) during treatments and for ten minutes after the uranium has been dissolved. The radioactivities of the krypton and xenon trapped in charcol are measured by a multi-channel gamma ray spectrometer. Their gamma-ray spectra are shown in Fig. 2. The cooling periods to minimize the interference of precursor and radioactitvity of the other nuclides are found to be 1.5 and 4 days for xenon-135 and xenon-133, respectively. The use of one of these nuclides depends on the nature of the sample and the function of the measuring instrument, and the cooling period is therefore determined by the nuclide thus selected.

Preparation of the Heating Curve and X-ray Diffraction Measurement. — In the emanation method, the samples containing radioactive rare gases were heated at a constant rate and the radioactivity of the escaping rare gases was measured (heating curves), or the samples were heated at various temperatures and kept at these temperatures while the changes in escaped radioactivity with time were followed (isothermal curves). In the present

TABLE I. THE HEMATITE SAMPLES AND THEIR PREPARATION METHODS

Sample No.	Chemical form	Preparation method
1	α-Fe_2O_3	Dehydration of α-FeO·OH at 250°C
2	α-Fe_2O_3	Dehydration of α-FeO·OH at 300°C
3	α-Fe_2O_3	Thermal decomposition of $FeSO_4\cdot7H_2O$ at 780°C
4	γ-Fe_2O_3	Oxidation of Fe_3O_4 at 250°C
5	γ-Fe_2O_3	Pure γ-Fe_2O_3

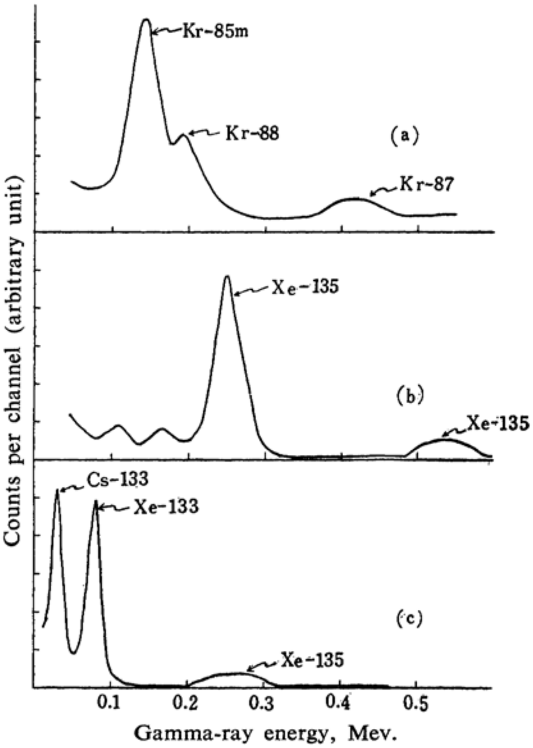

Fig. 2. Gamma-ray spectra of the fission product rare gases.
(a) 2 hr. irradiation and 8 hr. cooling.
(b) 2 hr. irradiation and 1.5 day colling.
(c) 2 hr. irradiation and 5 day cooling.

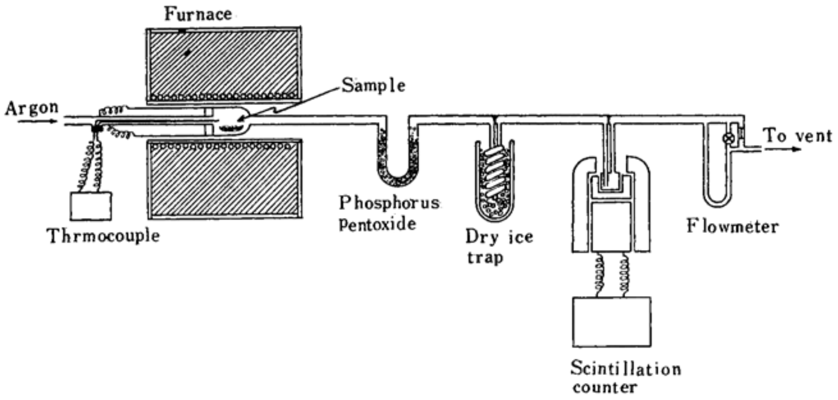

Fig. 3. Schematic diagram of the heating apparatus.

work, the crystal structure change of γ-hematite to α-hematite is studied by the heating curve. An X-ray diffraction method is also employed to identify the crystal structures. The samples of hematites to be examined are shown in Table I.

Two hundred milligrams of thin film of formvar, in a small size, containing uranium dioxide of which the weight ratio to formvar is 1 : 5 was mixed with 500 mg. of hematite and irradiated by thermal neutron flux $\sim 5\times10^{11}$ n/cm² sec. for 2 hr. in an experimental hole of JRR-1 reactor. Then the fission recoil energy enables the fission products to be caught by the surrounding solid powder through the film[4-6]. After 1.5 days' cooling ethyl alcohol was added to the sample and the solid powder retaining fission products was separated by a wire gauze and filter paper and was dried. The solid powder was placed in a quartz boat in a quartz tube which was connected to a phosphorus pentoxide drying tube, a dry ice trap for radioactive iodine, a counting cell inserted into an NaI scintillation crystal well of a γ-ray spectrometer and a flow rate meter, in the order mentioned. The schematic diagram of the apparatus is shown in Fig. 3. Solid powder was heated by a furnace at a rate 5°C/min. in a current of argon (100 ml. per min.). The radioactive xenon-135 escaping from hematite was carried by argon and the radioactivity was measured with the scintillation counter. Plots of the radioactivity of xenon-135 escaped from the sample versus temperature are shown in Fig. 4.

The correlations between the observed peaks in the heating curves and the crystal structure changes were studied by the high temperature X-ray diffraction method at temperatures below and over the temperatures where the peaks appear. γ-Hematite samples (Nos. 4 and 5) were investigated by the continuous recording method, by the use of the peaks (220) of γ-hematite and (104) of α-hematite. The charts are shown in Figs. 5 and 6.

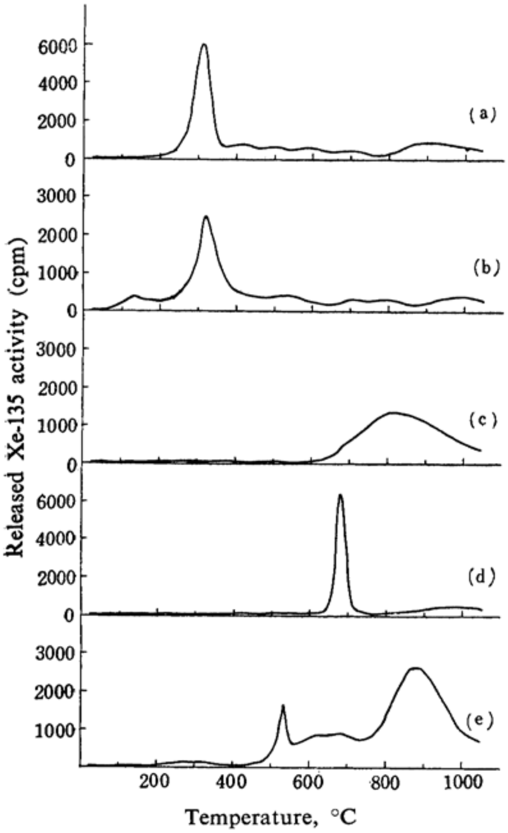

Fig. 4. Heating curves (5°C/min.) of hematite samples.
- (a) No. 1 α-hematite sample.
- (b) No. 2 α-hematite sample.
- (c) No. 3 α-hematite sample.
- (d) No. 4 γ-hematite sample.
- (e) No. 5 γ-hematite sample.

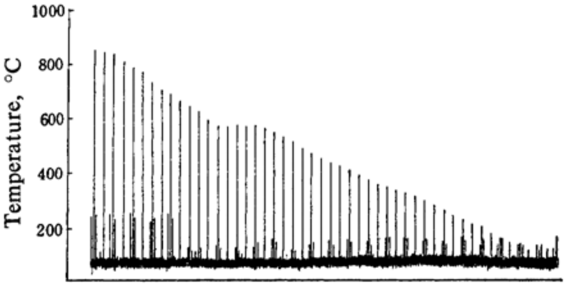

Fig. 5. Continuous recording chart of high temperature X-ray diffraction of No. 4 γ-hematite sample. Successive vertical lines indicate temperature.

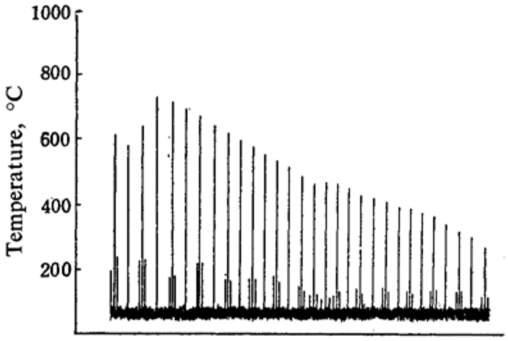

Fig. 6. Continuous recording chart of high temperature X-ray diffraction of No. 5 γ-hematite sample. Successive vertical lines indicate temperature.

Results and Discussion

The peaks in the heating curves of Nos. 1 and 2 samples are considered to be related to the dehydration of FeO·OH, although the X-ray diffraction chart shows that the No. 2 sample is in α-hematite form at room temperature. In the heating curve of No. 3 sample, no sharp peak is observed because no change

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[4] R. Wolfgang, *J. Inorg. Nucl. Chem.*, **2**, 180 (1956).

[5] R. Henry and C. Herczeg, UNESCO/NS/RIC/14 (1957).

[6] T. Nakai and S. Yajima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1267 (1958).

in structure takes place. The slow ascendant of the curve probably shows that the xenon trapped in the dislocation of the crystal is released. The samples of Nos. 4 and 5 are identified to be γ-hematite at room temperature by the X-ray diffraction method but their heating curves of Fig. 4 are considerably different from each other. The charts of the continuous recording method of Figs. 5 and 6 show that peaks at 680°C and 530°C are the temperatures of the crystal structure change of γ-hematite of samples Nos. 4 and 5 to α-hematite, respectively. The difference of their crystal structures might be investigated in detail by other methods, e. g., electron diffraction method.

The heating curves of the emanation method will suggest the temperature at which the crystal-structure change, dehydration and decomposition occur and also the detailed difference of the crystal structure for which the X-ray diffraction method does not give sufficient informaton. The heating curves may also suggest the possible existence of the dislocation of the crystal.

On the basis of the following reasons, the proposed method will promise a future development in various fields of the study.

1) This method will be applicable to many solids because the samples are prepared without chemical treatments.

(2) Different radioactive rare gases can be used at the same time. For example, prior to the reaction, if different nuclides of radioactive rare gas were retained in the reactants, the more detailed knowledge of the reaction between solids would be obtained.

3) When most of the rare gas is released at the first peak, it is possible to investigate the emanation at the higher temperature above the peak by means of the decay products of the precursor.

The radiation damage of the crystal will be negligible because the radioactivity of the fission rare gases is detected very sensitively and the sample does not require so much irradiation, as radiation damage occurs. The fission products captured in the solid will be also negligible as impurities.

The proposed method will be useful for the studies of crystal-structure change, reaction between solids and other problems of physical chemistry when the X-ray diffraction method and electron diffraction method are employed at the same time.

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