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Magnetometric and Röntgenometric Studies of Pyrrhotite from the Kawayama Mine, Japan

By

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with 4 Tables, 26 Text-figures

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Abstract: Pyrrhotites (FeSx), of various compositions, collected chiefly from the Kawayama mine have been subjected to investigation. The value of saturation magnetization (σ_s) depending on the composition is in the range of $0 \sim 22$ e.m.u./gr. for $x=1.066 \sim 1.142$. It is deduced from a maximum value of saturation magnetization that Fe^{3+} ions are present mainly in the B layer and partly in the A layer of the Bertaut type structure. Natural specimens of pyrrhotite are on the basis of the magnetic susceptibility versus temperature (σ-T) relations classified into four types: 1) Type I, with no α- and γ-transformations above the room temperature and very small σ in magnetic susceptibility, 2) Type II, with well defined γ-transformations, 3) Type III, showing γ-transformation superposed on σ-T curve of Weiss type, and 4) Type IV, with σ-T curve of Weiss type. The saturation magnetization and composition range are $\sigma_s \lesssim 1$ and $1.05 \lesssim x \lesssim 1.09$ for Type I, $1 \lesssim \sigma_s \lesssim 6$ and $1.09 \lesssim x \lesssim 1.11$ for Type II, $6 \lesssim \sigma_s \lesssim 15$ and $1.11 \lesssim x \lesssim 1.13$ for Type III, and $\sigma_s \gtrsim 15$ and $x \gtrsim 1.13$ for Type IV respectively.

A simple relation is found between the temperature of γ-transformation and the composition, making possible to determine the composition of natural pyrrhotite belonging to the Type II.

It is clear that the central part of the related ore deposit is occupied by pyrrhotite with smaller value of σ_s corresponding to that of the mineral with less iron deficiency than for that of the outer part.

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I. INTRODUCTION AND ACKNOWLEDGEMENT

Within the seemingly bedded deposit of cupriferous iron sulfides, in the Kawayama mine, Yamaguchi Prefecture, pyrrhotites are found widely distributed, and seem to offer an opportunity of making it possible to study their occurrence from both mineralogical and ore-depositary point of view.

Occurrence of pyrrhotite as an important mineral in the ores is mainly limited within the deposits classified genetically by EMMONS (1940) into those produced magmatically through segregation, through contact metamorphism and through formation of vein in the depth, and by LINDGREN (1933) into those formed magmatically, pyrometasomatically and hydrothermally. Whereas SCHWARTZ (1937) concluded in his discussion on the paragenesis of pyrrhotite with other sulfides that the mineral is most commonly associated with chalcopyrite, pyrite, sphalerite, arsenopyrite, magnetite, galena and so on in descending order.

Denomination for pyrrhotite of the berthollide type is restricted to in the cases of hexagonal or monoclinic phase and the mineral in question has the approximate composition of FeS with less amount of iron than is indicated by this formula. The hexagonal and monoclinic forms are commonly encountered, either together or singly, in studies of ores. It is questionable whether the two may be polymorphs or the inversion product from one to the other in association with compositional change. It is known that a defect structure contributes to its own specific property and causes certain deviations from the other simple hexagonal type of NiAs. Stoichiometric FeS is known as antiferromagnetic troilite occuring mainly in meteorite. Recently, as for the stoichiometric composition of mackinawite (approximately FeS) some problems have been presented (CLARK, 1964, 1966 ; TAKENO, 1965).

On the other hand, pyrrhotite has interesting and complicated properties from magnetic, thermo-analytical, electrical and crystallographical aspects. Of all, the magnetic property and the behavior at the spacing d (102) (for hexagonal type) observed in the range of 2θ between 43.5° and 44.0° in the case of CuK_α radiation will be dealt with in the present paper.

Concerning the magnetic properties, it is well known that the pyrrhotite represented by the formula FeS_x $(1.0 \leqq x \leqq 8/7)$ is antiferromagnetic in the range of $1.0 \lesssim x \lesssim 1.1$ (50.0 ~ 47.6 atomic per cent Fe) and ferrimagnetic in the range of $1.1 \lesssim x \lesssim 8/7$ (47.6 ~ 46.7 atomic per cent Fe) as well as in the range of x between the above two $(x \sim 1.1)$ (47.6 atomic per cent Fe) at certain restricted temperatures.

As was already reported in the previous work, the main ore bodies of the Kawayama mine consist of sulfides and are, in general, bedded in form, nearly parallel to the schistosity recognized in the bedding of the country rocks composed of the semischist belonging to the Sangun-Motoyama metamorphic group. The ores consist of pyrrhotite associating a little amount of sphalerite, chalcopyrite, marcasite, galena and cubanite.

The natural specimens of hexagonal and monoclinic pyrrhotites denoted for convenience's sake as FeS_x in chemical formula have been collected mainly from the lower ore deposit of this mine and subjected to magnetic and röntgenographical experiments.

This paper includes some parts of the results of recently published paper reported by the present writer and his co-workers (TAKENO *et al.* 1966).

ACKNOWLEDGEMENT: The writer wishes to express his greatful appreciation to Professor Yoshiharu UMEGAKI of the Hiroshima University for his invaluable helps and instructive advices during the work as well as for his revision of the manuscript. The writer also wishes to express his gratitude to Emeritus Professor S. IMAMURA and Professor G. KOJIMA of the same University for their continuous guidance and encouragement. He is also much obliged to Professor T. KAMIGAICHI of Laboratory of Physics, Department of the General Education, Hiroshima University, under whose guidance and valuable advices the measurements of magnetism have been carried out, and to Lecturer K. MASUMOTO of Kure Technical College for his help in measurements of magnetism. Thanks are also due to Drs. Y. KINOSAKI of the Onoda Cement Co. Ltd., A KATO of the National Science Museum, Tokyo, K. HIDE, A. SOEDA of the Institute of Geology and Mineralogy, Hiroshima University for their valuable advices, and to the geologists of the Kawayama Mining Office for their assistances in carrying out his field work.

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II. PREVIOUS WORK FOR THE EXPERIMENTAL BASIS

The complexity of magnetic properties, structure and solid solution of pyrrhotite was attested by voluminous literatures appeared in the last 50 years. Recent works has also placed emphasis on the similar themes as to natural pyrrhotite.

ALSÉN (1925) was the first who assigned the structure of pyrrhotite to the arrangement now known as that of the NiAs-type (B8). HÄGG and SUCKSDORFF (1933) demonstrated that the compositional variations related to omission of Fe atom sites normally occupied in the NiAs-type structure. They also reported that in synthetic compounds with composition ranging from $FeS_{1.00}$ to $FeS_{1.07}$ (50.0 to 48.3 atomic per cent iron), the simple cell is converted to a supercell through distortion. HARALDSEN (1941), proposing a phase diagram for the system, showed that the superstructure inverts to a NiAs-type structure at 138°C. BERTAUT (1956) subsequently determined the crystal structure of two troilite phases and found the superstructure to be caused by small displacement of Fe atoms normal to *c* and that of S atoms parallel to *c*.

GRONVØLD and HARALDSEN (1952) reported that the simple NiAs cells are predominnant at room temperature in the cases of synthetic compounds from $FeS_{1.075}$ to $FeS_{1.12}$ ($48.2 \sim 46.73$ atomic per cent iron), while the monoclinic ones are common in the cases of those with more iron-deficiency ranging from $FeS_{1.12}$ to $FeS_{1.20}$ ($46.73 \sim 45.44$ atomic per cent iron). The latter modifications, e. g. with $a=5.94$

Å = B, $b = 3.43$ Å = A, $c = 5.68$ Å = C and $\beta = 90.37°$, have been confirmed by BYSTRÖM (1945) concerning the natural magnetic pyrrhotites from a number of Swedish localities. BUERGER (1947) observed the pyrrhotite crystals exhibiting a superlattice with $a = 2$A and $c = 4$C from several localities. Aside from their total composition, they were assumed to be deficient in iron content by virtue of their ferromagnetism. Extinctions belonging not to any space group in the pattern might be ascribed to the specimens with twinning, whereas pyrrhotites are really to be monoclinic or orthorhombic in symmetry. Subsequent study carried out by WUENSCH (1963) indicates the same sample from Morro Velho to be pseudohexagonal and also the precession photographs suggesting a superstructure seemingly with two and four times A and C dimensions of NiAs-type substructure, justifying the earlier work by BERTAUT (1953) who proposed a monoclinc superlattice and gave $a = 2$B and $c = 4$C for both cells.

Recently, CARPENTER and DESBOROUGH (1964) examined the range in solid solution and the structure for troilite and pyrrhotite in natural occurrence. They grouped the mineral FeS_x (pyrrhotite group) into three forms, *i. e.* 1) hexagonal supercell with $A = 2a$ and $C = 5c$ of the NiAs-type structure observed in pyrrhotite ranging in composition from about $FeS_{1.083}$ to $FeS_{1.128}$ (48.01∼46.99 atomic per cent Fe), 2) monoclinic supercell with $A = 2a$, $B = 2b$ and $C = 4c$ and 3) troilite with $a = \sqrt{3}A = B$, and $c = 2C$.

On the other hand, as was shown by GRØNVOLD and HARALDSEN (1952), the cell dimension of synthetic hexagonal pyrrhotite decreases regularly with decrease of its iron-to-sulfur ratio. Thus, based on the x-ray determination curve relating d (102) to iron content ARNOLD (1956) payed attention to that pyrrhotite may contain intergrowth lamellae of another phase and the related curve is suggestive for finding the correct value of bulk compositions only if the specimen is homogeneous. Subsequently ARNOLD and REICHEN (1962) showed that a number of natural pyrrhotite in composition ranging from $FeS_{1.084}$ to $FeS_{1.142}$ (47.98 to 46.68 atomic per cent Fe) have been satisfactorily determined through d(102) measurements.

The presence of Co, Ni and other elements contained as solid solution in pyrrhotite is reasonably considered to give influence on the d (102) spacing, whereas the fact is that 2% of (Ni+Co) in weight and about 0.6% of Co present in pyrrhotite have not caused an appreciable change for the d (102) values (ARNOLD and REICHEN, 1962). The concentration of these elements in natural pyrrhotite is usually below these limits (FRYKLUND and HARNER, 1955). As for the minor elements in pyrrhotite from the Kawayama mine, TAKENAKA (1954) spectroscopically recognized no traces of Ni and Co but certain amounts of Cr, Cu, and Ag etc.

The x-ray method, a rapid and convenient way for determining the composition of pyrrhotite, is more advantageous than the chemical methods since high-grade separation is not necessary for obtaining accurate results. Arnold's method related to d (102) has been applied to the specimens in the ore bodies of some special types by many investigators and reached the remarkable results (e.g. TSUSUE, 1962, CLARK, 1964).

It would be desirable to extend the pyrrhotite geothermometer in relation not only to the hexagonal modification (ARNOLD, 1962) but also to the monoclinic one. GRNVOφLD and HARALDSEN (1952) reported on the ground of their work on synthetic materials that low-temperature monoclinic pyrrhotite inverts to the hexagonal phase at about 320°C. With attempt to use monoclinic pyrrhotite as a geothermometer, ARNOLD and REICHEN (1962) heated pyrrhotite at 600°C for 18 hours. Recently, KULLERUD *et al.* (1963) reported the complete conversion of monoclinic pyrrhotite to the hexagonal form when heated for 0.1 hour at temperatures above 320°C.

HARALDSEN (1964) and LOTGERING (1956) found in their investigations of the synthetic FeS_x with various contents of x that the magnetic behaviors are sensitively influenced with an excess of sulfur content and the magnetic susceptibility versus temperature curve exhibits the knicks at such temperatures as T_α (90°～140°C), T_β (325°C) and T_γ (180°～250°C) corresponding to α-, β-and γ-transfromations respectively. $FeS_{1.00}$, the stoichiometric composition, indicates two knicks, of which one is related to α-transformation and the other to β-transformation, and T_β shows no changes with increasing sulfur content while T_α shifts to the lower-temperature sides with increase of x and disappears at $x=1.09$ (47.85 atomic per cent Fe). γ-transformation is also recognized between α-and β-transformation at $x=1.06$ (48.54 atomic per cent Fe) and shifts to the higher-temperature side with increase of x and disappears at $x=1.12$ (47.17 atomic per cent Fe) (See FIG. 15).

The crystal structure of the mineral in association with magnetic properties has been studied by JUZA *et al.* (1932), HÄGG (1933), HARALDSEN (1939), UEDA *et al.* (1950) and BERTAUT (1953). These results are briefly summarised as follows; The crystal structure of FeS_x ($1.00 \leqq x \lesssim 1.14$) is of hexagonal NiAs type and reveals no essential change at T_α, T_β and T_γ. But a superlattice structure is found at the temperature lower than T_α and disappears at x of more than 1.06. This superlattice structure has a hexagonal cell with $a=5.968$Å and $c=11.74$Å for $x=1.00$ and can be derived through small displacement of iron and sulfur atoms from the NiAs type. In general, the lattice constant c contracts gradually with increase of sulfur content in spite of no remarkable variation in the lattice constant a. On the other hand, c contracts abruptly, *i. e.* shows an anomalous contraction, with increasing temperature (especially at T_α) in opposition to a slow expansion of a. As for the mechanism of these transformations, several explanations have so far been given by many workers.

YOSHIDA (1951) and HIRONE and TSUYA (1951) pointed out that the stoichiometric iron sulfide has a magnetic structure in which the spins of ferrous iron are aligned parallel in each of two equivalent sublattices formed by odd- and even-numbered c-planes respectively and are coupled antiferromagnetically between both sublattices, and that β-transformation is due to the order-disorder change in such a spin arrangement. On the basis of this magnetic structure, BERTAUT (1953) explained the conversion of ferro- to ferrimagnetic nature in the case of $x \geqq 1.10$.

With respect to the magnetic characters of natural pyrrhotite, several investigations have been given in the geological literatures. HAYASE *et al.* (1963) and SHIBUYA (1966) studied the temperature dependency on magnetism of natural pyrrhotite and classified into three types, *i. e.* the first, the peak-type pyrrhotite, bearing the weakest magnetism characterized by a single sharp peak at 220°C on σ–T (magnetic susceptibility versus temperature) curve, the second having the strongest magnetism with a tendency of ordinary Weiss-type on σ–T curve and the third indicating an intermediate tendency between the above two in intensity of magnetization and σ–T curve.

III. EXPERIMENTAL PROCEDURES

A. SPECIMENS USED IN THE EXPERIMENTS

More than 150 specimens of natural pyrrhotite provided for these experiments were collected mostly from some levels such as -110, -140, -180, -210 and -240m levels of the Kawayama mine, as are illustrated in the underground geological maps of the mine (FIGS. 23, 24 and 25).

For comparison of the data with one another, the specimens from some types of the ore deposits were also used. Their localities and the investigators presenting the specimens are as follows:

1. Outokumpu mine, Finland (Stope U 27) (Professor T. TATUMI of the Tokyo University).
2. Makimine mine, Miyazaki Pref. (Chigusa-adit) (Mr. T. NAGAI of the Makimine Mining Office).
3. Yanahara mine, Okayama Pref. (L. 17 of the main ore body) (Dr. S. HIGASHIMOTO of Geological Survey of Japan).
4, Tsumo mine, Shimane Pref. (Maruyama ore body, L. 25) (Mr. T. SHINMEI of Nichibei Rozai Co. Ltd.).
5. Besshi mine, Ehime Pref. (Nakazo adit) (Dr. K. HIDE of Institute of Geology and Mineralogy, Faculty of Science, Hiroshima University).
6. Nonowaki mine, Tokushima Pref. (Middle ore body, L. 90) (Mr. M. NAKAGAWA of Institute of Fukada Applied Geology Co. Ltd.).
7. Tarô mine, Iwate Pref. (Lower L. 6).
8. Kômori mine, Kyoto Pref. (Raiko No. 1, -380mL.).
9. Akagane mine, Iwate Pref. (Ist sub-L. of the 2nd adit in the six ore body).
10. Ômine mine, Iwate Pref. (No. 2 adit).

Each specimen, about 2 × 2 × 1 cm^3 in size, was picked up from the polished sections under the reflection microscope with taking care of the mineral pragenesis.

B. MAGNETIC MEASUREMENTS

About 10～30mg of pyrrhotite, pulverized to approximately 250～350 mesh in grain size in order to avoid heterogeneity in magnetization, were subjected to magnetic measurements.

1. Apparatus used for experiments

The measurements were carried out with aid of the magnetic balance similar to that described by HIRONE *et al.* (1954).

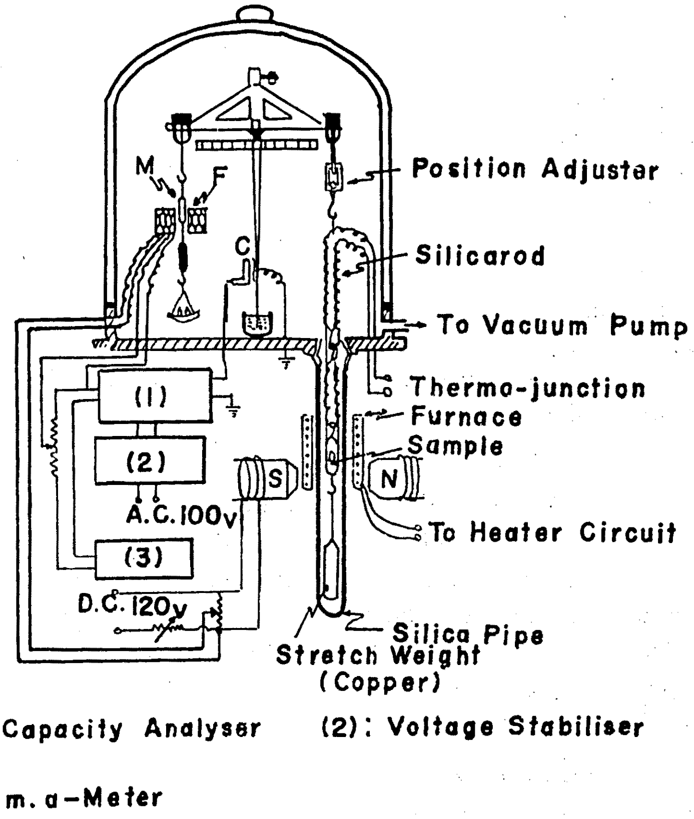

FIG. 1. Schematic diagram showing the magnetic balance (given by HIRONE *et al.* 1954, but partially modified by the present writer).

If a sample with the ferromagnetic or other magnetic property is suspended in an inhomogeneous magnetic field, the force f acting on the sample is given by

$$f=\chi\cdot m\cdot H\frac{\delta H}{\delta Z},$$

where χ is the susceptibility, m the mass of the sample, and $\frac{\delta H}{\delta Z}$ the gradient of the magnetic field H in the vertical Z direction. The field gradient was determined by using the Mohr's salt as the reference specimen after each series of measurements. In this instrument shown schematically in FIG. 1 the sample is hung from one end of the beam of an ordinary weighing balance, while from the other end a small needle magnet M is hung and partially inserted into a center hold of a small solenoid F. The force acting on the sample is to be compensated from the mutual force between the needle magnet and magnetic field produced by the compensating current through the solenoid F. The compensation current can be produced by a capacity analyzer connected with pickup condenser C placed on the lower end of the balance pointer.

When the sample hung at a little upper part in the center of the magnetic field is attracted in the magnetic field of the electromagnet, the equilibrium of the balance is broken in a moment, and at the same time the capacity of the pickup condenser C decreases. Then the needle magnet M is attracted downward because of the increased current in the feedback coil F. Through these processes the balance is recovered instantly. The change of the specimen's position during this process is negligibly small (less than lmm at an ordinary state). The current in the feedback circuit is measured by a milliameter, the reading of which directly points to the change of magnetic susceptibility χ of the sample. All of the moving system in the apparatus is enclosed in an evacuated chamber (about 10^{-3}mmHg) in order to be freed from disturbance due to the buoyancy change of the sample and the air flow around the balance.

2. *Determination of σ-T (magnetic susceptibility versus temperature) curves*

Sample collected under the microscope are sealed in the silica-glass tubes evacuated down to about 10^{-6}mmHg for protecting them from oxidation. Each temperature, at wich the specimens were held, was measured by means of an almel-chromel thermocouple. The varying rate of temperature was about 100°C per an hour either on heating and cooling or on reheating and recooling. On determining the σ-T relation, the electric magnet was equipped to be capable of operating at 5000 Oe.

3. *Determination of the saturation magnetization (σs)*

Owing to impossibility of attaining the perfectly saturated state of magnetism for the specimens with these instruments 2,250, 3,970, 5,000, 5,770, 6,250 and 6,700 Oe in intensity of the magnetic field were respectively taken, and the $\sigma - 1/H$ curves obtained were extrapolated to the region $1/H \rightarrow 0$ in order to determine the saturation magnetization (σs). Some examples are shown in FIG. 2.

C. X-RAY APPARATUS AND CONDITIONS

X-ray apparatus provided for the research was GX-2B diffractometer manufactured by Shimazu Man. Co. Ltd., to which the autoscaler, recorder, powerful transformer putting out 60KV in maximum and so on were attached. The method of the experiments was similar to that described by UMEGAKI *et al.* (1963). Namely, the paste of the pulverized specimen (finer then 250 mesh in grain-size) was kneaded with nitrocellose diluted in amyl acetate, flattend on the glass plate and allowed to be dried up in the air.

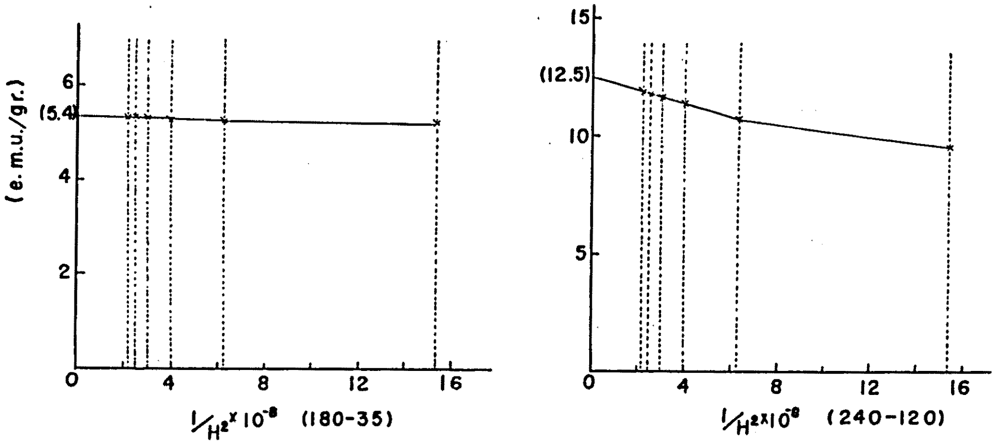

FIG. 2. Explanative curves for determining saturation magnetization.

The spacings of specimens were determined with reference to the values for d (102) and d (112) of qurtz used as a sort of indicator standardizing the spacings.

Taking into account of the counting miss ascribed to the electronic cirquit of G. M. counter, probable errors in numbers of pulses, opening angle of the slit, effect of duration of diffractive rays and the characteristic of the appartus used, conditions suitable for the experiments were kept constant as follows:

X-ray: CuK$_{\alpha}$, time constant: 5 sec for 500cps (excepting the special cases), scanning speed: 1° (2θ)/min (excepting some cases), rotating speed of chart: 1 cm/min, divergent slit: 1.5 mm in width, and receiving slit: 1.2 mm in width. In measurements of d (102) for hexagonal form or d (202) and d ($\bar{2}$02) for monoclinic form, x-ray diffraction figures were recorded between 42° and 45° in 2θ scanned from low to high angles at least three times for each specimen on charts. 2θ for (102) (for hexagonal) was finally determined from the average values concerning three to five times measurements. When the reflections of (102) for hexagonal pyrrhotite were complicatedly splitted or obscure the peaks appeared at the half of the height on the center of the width were taken.

IV. EXPERIMENTAL RESULTS FOR MAGNETIZATION

A. SATURATION MAGNETIZATION (σs)

In the light of the procedures mentioned above, the values for σs were measured as to all specimens, and a part of the results ranging from few to about 22 e.m.u./gr. are listed in table I (p. 135).

1. *Relation of σs to chemical composition*

The data for σs have so far been not so much systematically given, exculusive of those reported by LOTGERING (1956) and HIHARA (1960). The present writer has estimated the values for σs in conjunction with composition of FeS_x from the σ-T or $\frac{1}{\chi}$-T curves. As is illustrated in FIG. 3, inspection of these relations indicates a difficulty in determining the composition of pyrrhotite, especially when x is smaller than 1.10, and some possibility for estimation only in the range of $x \gtrsim 1.10$.

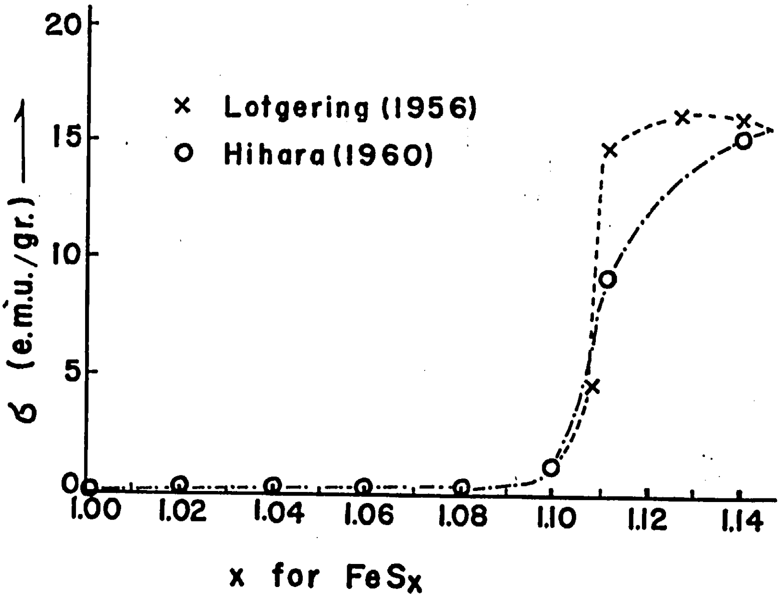

FIG. 3. Correlation diagram between the composition of FeS_x and saturation magnetization.

Usefulness of σs in association with σ-T relation determining the composition of the mineral will be described hereunder.

2. *Variation of σs*

FIG. 4 shows the distribution of σs for pyrrhotite specimens obtained from some parts on -140m, -180m, -210m and -240m levels of the Kawayama mine. General trend, characteristic as a whole, reveals two concentrated parts in the σs values: one is in the range of $0 < \sigma s < 4$ and the other in the range of $\sigma s > 16$.

Characteristics revealed in distribution of σs on each level are as follows:

a) 140mL. (The specimens taken are totalized 18 in number). The maximum is in the range of $0 < \sigma s < 4$ (45%) and a submaximum in the range of $12 \leqq \sigma s < 16$ (25%). In general, its frequency diminishes with increase of its values, as is typically appeared on -210mL.

b) -180mL. (Numbers of the specimens are 39). The maximum is in the range of

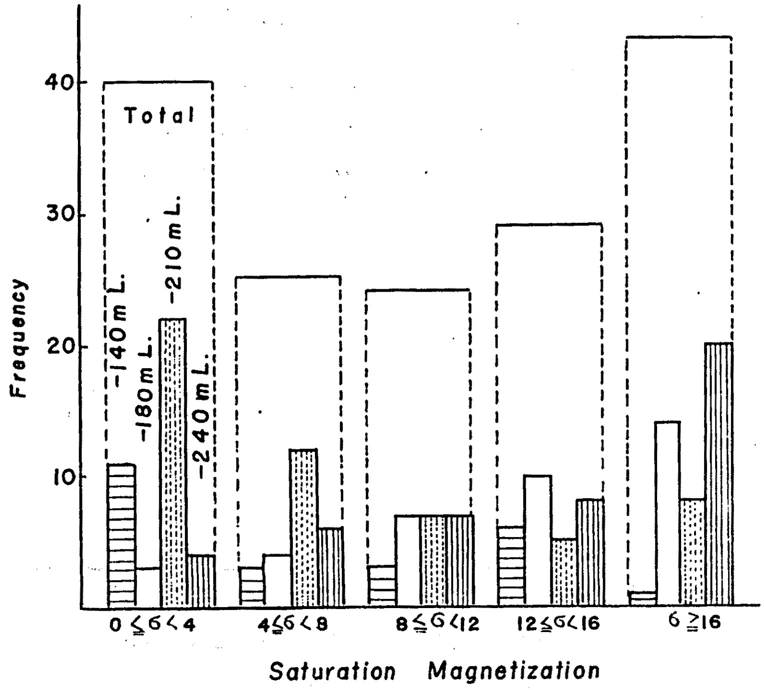

FIG. 4. Histogram showing the variation of the saturation magnetization of pyrrhotite from the Kawayama mine.

$\sigma s \geqq 16$ (35%) and its frequency typically increases as its values become larger.

c) -210mL. (Numbers of the specimens are 54). The maximum is in the range of $0 < \sigma s < 4$ (40%), and its frequency clearly decreases towards the parts with its the larger values.

d) -240mL. (Numbers of the specimens are 45). The maximum is in the range of $\sigma s \geqq 16$ (45%) and its frequency decreases towards the parts with its the smaller values.

The results mentioned above markedly show that σs is distributed heterogeneously either as a whole or on each level of the ore deposit, suggesting genesis of the related ore deposit with a sort of the concentrated center from certain kinds of ore solution probably indifferent with that of the wall rock though apart from general views as to formation of the 'Kieslager'.

3. *Relation of σs to the associated minerals*

As has been referred to in the preceding, it has become evident that the values for σs on each level bear a certain tendency in distribution. In addition, the writer (1963) has already pointed out the existence of differences in ore composition on each level, *i. e.*: pyrrhotite is predominant on -180mL., sphalerite on -240mL. and both on -210mL. FIG. 5 shows the relation between σs for pyrrhotite and contents of some others such as sphalerite and pyrite associate with pyrrhotite. In spite of the special features in σs and in composition of the associated ores on each level, there seems no conspicuous correlation between them. However, such tendency may be regulated by the sampling process of pyrrhotite, since the minerals in question were picked up especially from their concentrated parts as much as possible in each specimen. As shown in FIG. 5, it appears that σs becomes large (σs≳10) when pyrrhotite is associated with pyrite.

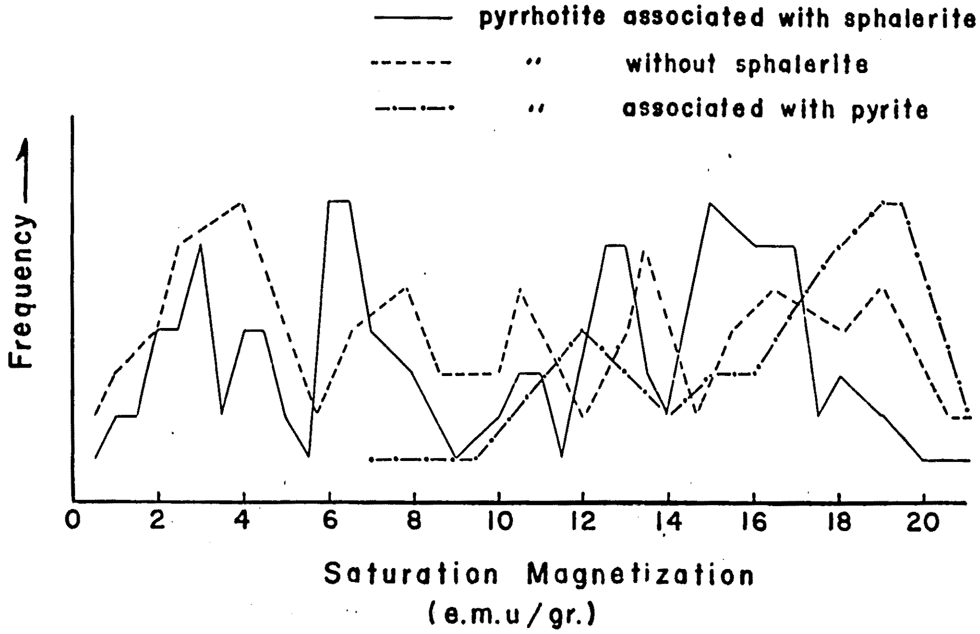

FIG. 5. Diagram showing the relation of saturation magnetization of pyrrhotite and paragenesis of the minerals.

B. σ-T CURVES OF NATURAL PYRRHOTITE

σ-T curves for more than 30 specimens were determined in relation to their compositions obtained more accurately than those from σs. Some of the data concerned are shown in FIGS. 6, 7, 8, 9, 10, 11, 12, 13 and 14.

1. *Variation in the type of σ-T curve*

The susceptibility versus temperature curves for all specimens are in accordance with the respective cases roughly divided into the following four types: (1) 1.05≲x≲1.09 (48.78~47.85 atomic per cent Fe), (2) 1.09≲x≲1.11 (47.85~47.39 atomic per cent Fe), (3) 1.11≲x≲1.13 (47.39~46.95 atomic per cent Fe) and (4) x≳1.13 respectively.

(a) *Type I with no α- and γ-transformations on σ–T curves and very small σ in magnetic susceptibility.*

This type is not dealt with in the classification proposed by HAYASE *et al.* (1963) and SHIBUYA (1966) who divided the natural pyrrhotite into three types besed chiefly on σ–T curves. FIGS. 6–(a) and 7 show the variation in magnetization of the natural specimens at the room temperature up to 430°C. Their values of σs are in the range from 1.2 (FIG. 6) to 1.9 (FIG. 7), and sulfur content deduced from σs are in the range of $x \gtrsim 1.07$, as has been referred to already. Moreover, these two σ–T curves display none of knicks either at 90°~140°C representing T_α or at 180°~250°C representing T_γ. The lack of α- and γ-transformations on the curve indicates the sulfur content x in FeS_x to be larger than 1.07 and smaller than 1.12. These curves obtained on cooling, reheating and recooling almost coincide with each other in both FIGS. 6 and 7, suggesting their correspondence to those of $FeS_{1.09}$ (47.847 atomic per cent Fe) reported by HIHARA (1960) (Fig. 6–b). This type of σ–T curve is recognizable in the specimens of 140–124 (σs$=0.1$). The specimen from Kômori mine (σs$=0.8$) is also of this type. All specimens of this type are of less than 1 e.m.u./gr. in σs. As are clear in FIGS. 6–(a) and 7, the initial heating curves exhibit larger values

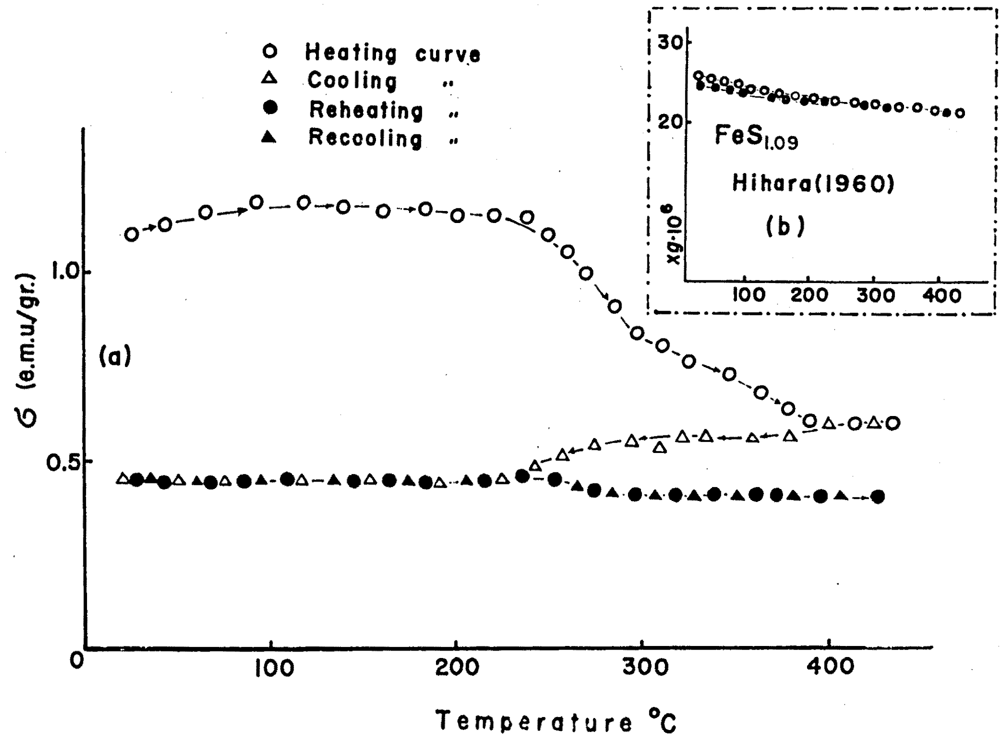

FIG. 6. Variation of magnetization of natural pyrrhotite (Kawayama mine, 210-16) (a) and synthetic $FeS_{1.09}$ (b) with temperature. It is to be noted that 30 χ-values (b) corresponds to 0.15 in σ-values (a). The arrows show the direction of temperature changes (Type I).

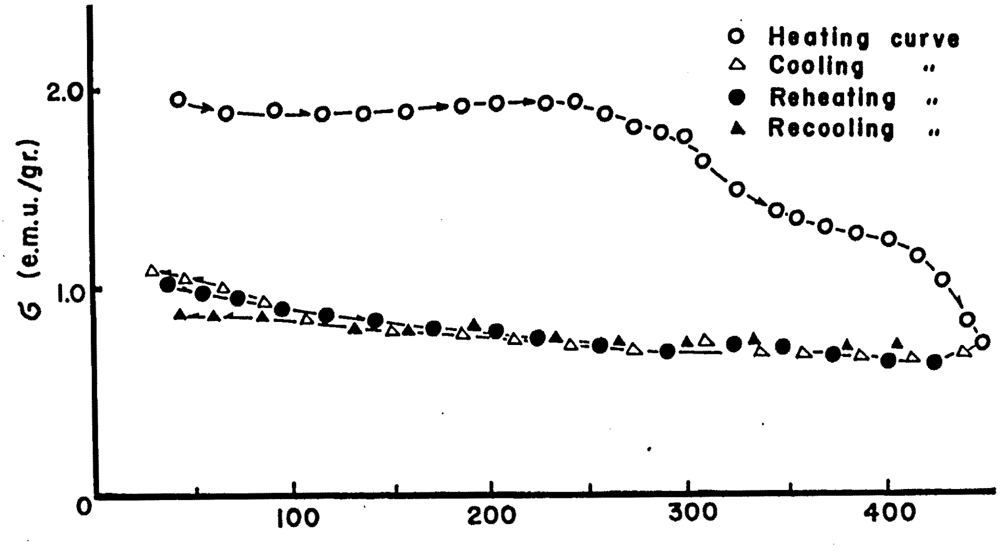

FIG. 7. Magnetization of natural pyrrhotite (Makimine mine, 1) as a function of temperature (Type I).

of magnetization than about 1 e.m.u./gr. probably due to the composition of natural pyrrhotite, because these specimens are considered partly to include pyrrhotite with a larger sulfur content than in the other parts. The reason why the large value of magnetization is not appeared on cooling, reheating and recooling curves may be ascribed to chiefly the ion diffusion caused by heat treatment degrading the average composition to about less than $FeS_{1.09}$. Thus, for classifying Type I in relation to σs its value is to be obtained after heating of the specimen, at least, at 400°C.

Of due significance is that the (102) interplaner spacings of this type point to the composition in the range of $1.066 \lesssim x \lesssim 1.091$.

(b) *Type II with well-defined γ-transformations*

This type probably corresponds to the "peak-type" reported by HAYASE *et al.* (1963) and SHIBUYA (1966) but their peak-type is limited to their specimens with a knick (T_γ) at 220°C on σ–T curves. FIGS. 8, 9 and 10 show the variations in magnetization of the Type II with temperature. All figures exhibit the λ-type manetization and a considerable variation of T_γ. In detail, for instance, T_{γ_1} on heating curve at 236°C in FIG. 9 and at 240°C in FIG. 10, T_{γ_2} on cooling curve at 230°C in FIG. 9 and at 225°C in FIG. 10, T_{γ_3} on reheating curve at 236°C in FIG. 9 and at 238°C in FIG. 10, and T_{γ_4} on recooling curve at 230°C in FIG. 9 and at 225°C in FIG. 10 are respectively to be remarked. In each case of these specimens T_β is in the range between 320°C and 325°C, as was already shown in the literatures. These specimens indicate 5.1 (FIG. 8), 2.1 (FIG. 9) and 2.2 e.m.u./gr. (FIG. 10) for σs respectively and the other ones belonging to this type smaller than about 6 e.m.u./gr., indicating the corresponding compositions in the range of $x \lesssim 1.11$. Based on measurement of the (102) spacings, type II reveals $1.093 \lesssim x \lesssim 1.111$ (47.78~47.37 atomic per cent Fe) in compostion.

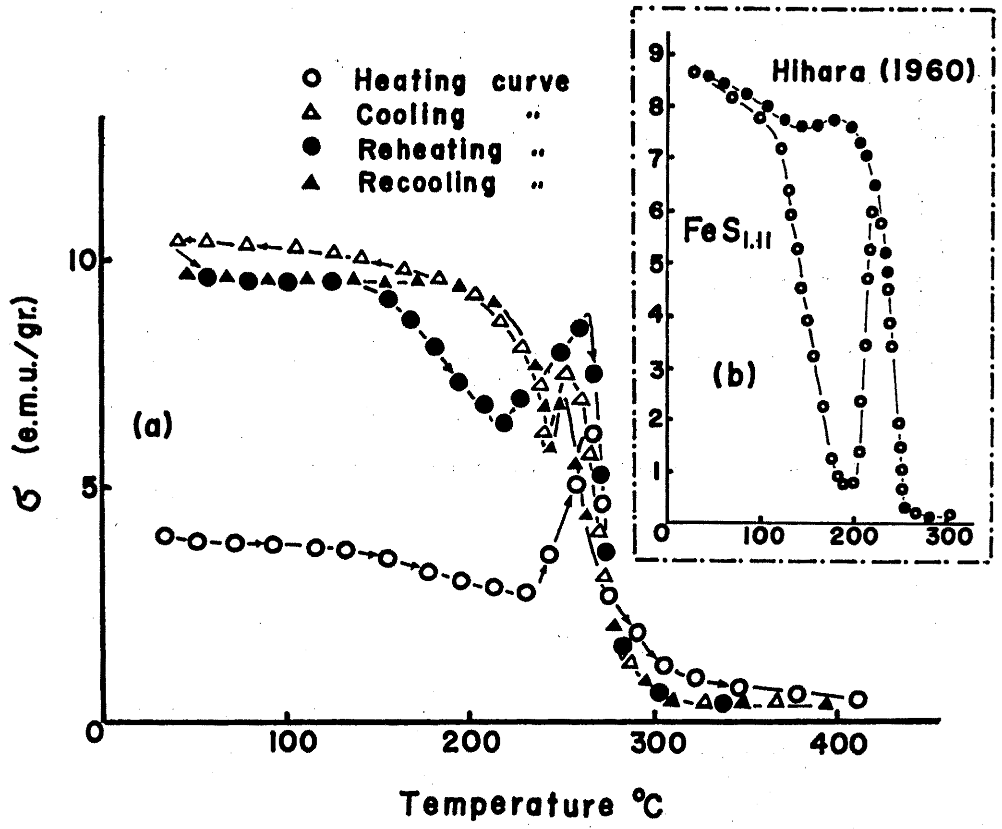

Fig. 8. Magnetization of natural pyrrhotite (Kawayama mine, 240-127)(a) and synthetic $FeS_{1.11}$ (b) as a function of temperature (Type II).

(c) *Type III with γ-transformation superposed on the σ-*T *curve of Weiss type*

This type may correspond to the "Mixed-type" reported by Hayase *et al.* As has already been stated, T_γ shifts to the higher-temperature side with increase of sulfur content x and disappears at $x=1.12$. Type III is considered as representing an intermediate one in composition between λ- and Weiss-type in magnetization. Fig. 11 and 12 show the variation in magnetization of the natural pyrrhotite from the Kawayama mine and Outokumpu mine, Finland with temperature. σ-T curves of the specimens 110-102, 110-109, 140-129, and 210-53 as well as those from the Tsumo and Akagane mine are of this type. Although T_γ of this type is lower than that of

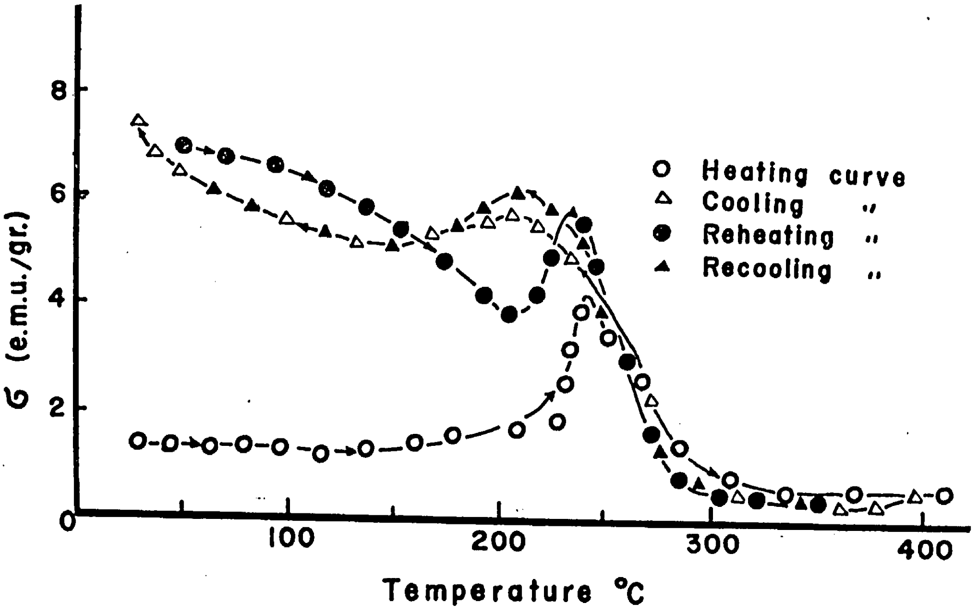

FIG. 9. Magnetization of natural pyrrhotite (Yanahara mine) as a function of temperature (Type II).

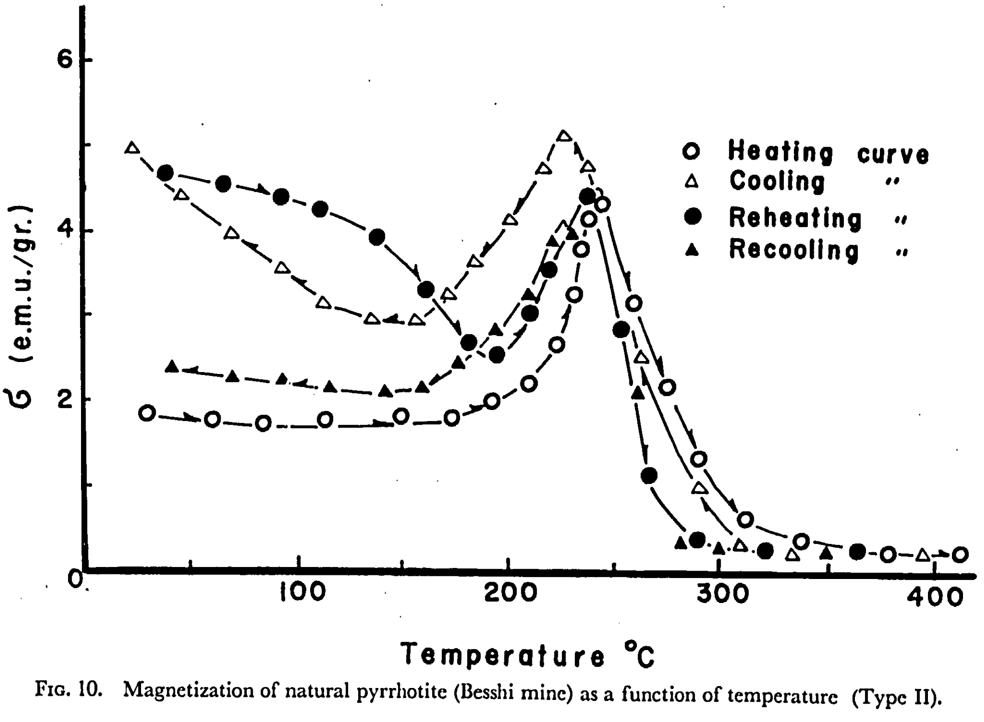

FIG. 10. Magnetization of natural pyrrhotite (Besshi mine) as a function of temperature (Type II).

Type II, the values of σs are larger than 15 e.m.u./gr. This suggests that x is in the range of $1.11 \lesssim x \lesssim 1.13$. In this type, T_β is clearly ascertainable at 320°C in the cases of all specimens.

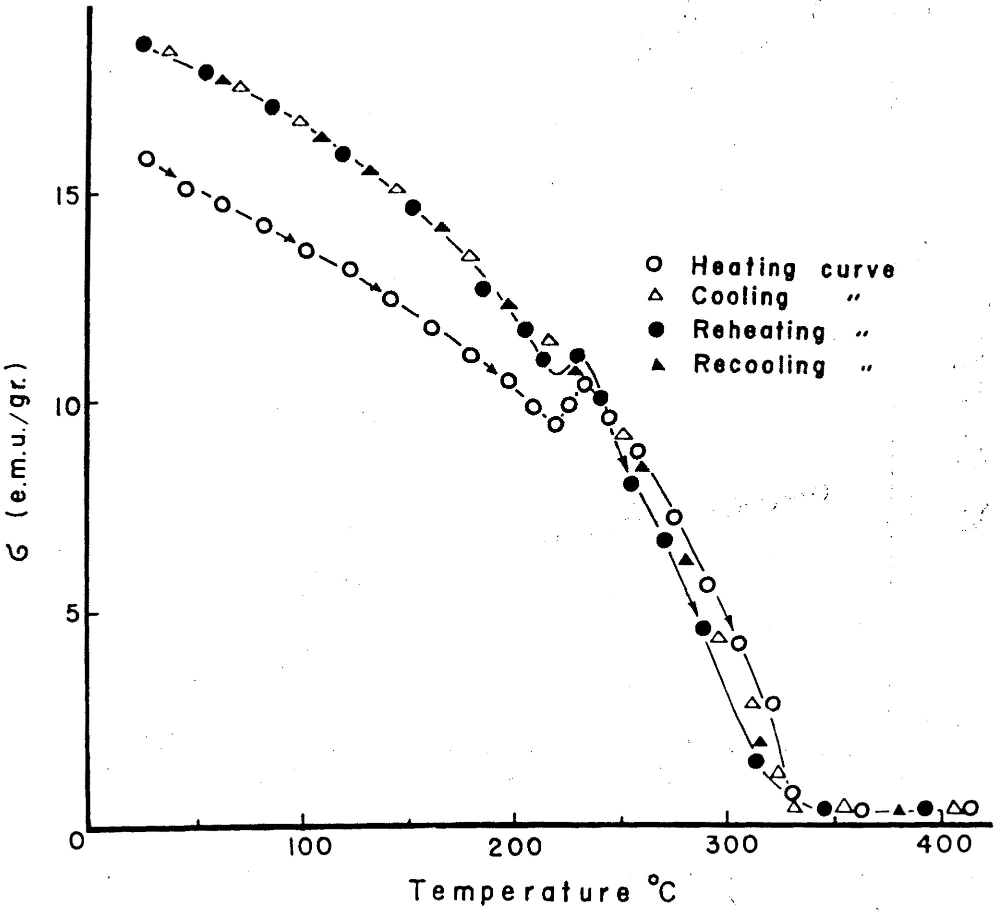

FIG. 11, Magnetization of natural pyrrhotite (Kawayama mine, 240-151) as a function of temperature (Type III).

In FIG. 11, T_γ is discernible at 234°C (on cooling or recooling curves). σ–T curve of this type with weak knicks at T_γ probably suggests that most of the specimens are almost in the range of $x \gtrsim 1.13$ corresponding to the Weiss-type magnetization aside from a few with $x \lesssim 1.13$ belonging to the λ-type magnetization.

On the other hand, the chemical compositions of this type, determined by d (102) method, are in the range of $1.109 \lesssim x \lesssim 1.134$ (47.42∼46.85 atomic per cent Fe).

(d) *Type IV with σ–T curve of Weiss type*

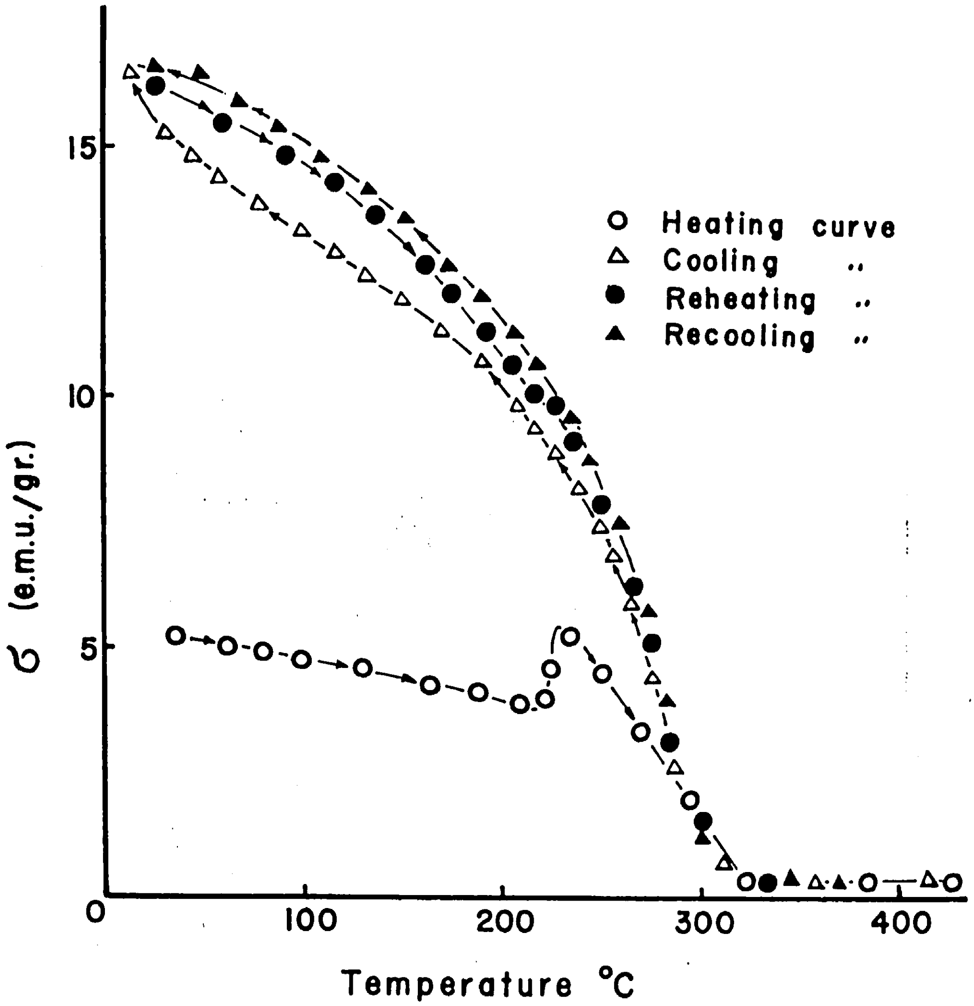

FIG. 12. Magnetization of natural pyrrhotite (Outokumpu mine) as a function of temperature (Type III).

HÄGG and SUCKSDORF (1933) recognized only the Weiss type of magnetization for the composition with sulfur content x of more than 1.12 in FeS_x. FIGS. 13-a and 14 show this type of σ–T curve though with a very slight knicks at T_γ. In all of the specimens under consideration, completion of the Weiss type without any knicks of T_γ is not observed but a very tiny one appears. This type is in the range of $\sigma s \geqq 16$, implying that most of the specimens are almost in the range of $x \gtrsim 1.13$ exclusive of a very few with about $x \lesssim 1.13$.

As for the x-ray powder diffraction patterns, most of the specimens of this type are monoclinic, but a few can not readily be interpreted as either monoclinic or hexagonal. Their chemical compositions deduced from d(102) after heating at 350°C for 0.1h are in the range of $1.132 \leqq x \leqq 1.142$ (46.904~46.685 atomic per cent Fe).

C. CORRELATION BETWEEN THE SULFUR CONTENT AND MAGNETIZATION

As has been described in the preceding, it seems rather difficult to determine the composition of pyrrhotite only from the σs values. So, in order to reach more accuracy in determing sulfur content of the minerals concerned, σ–T curves in connection

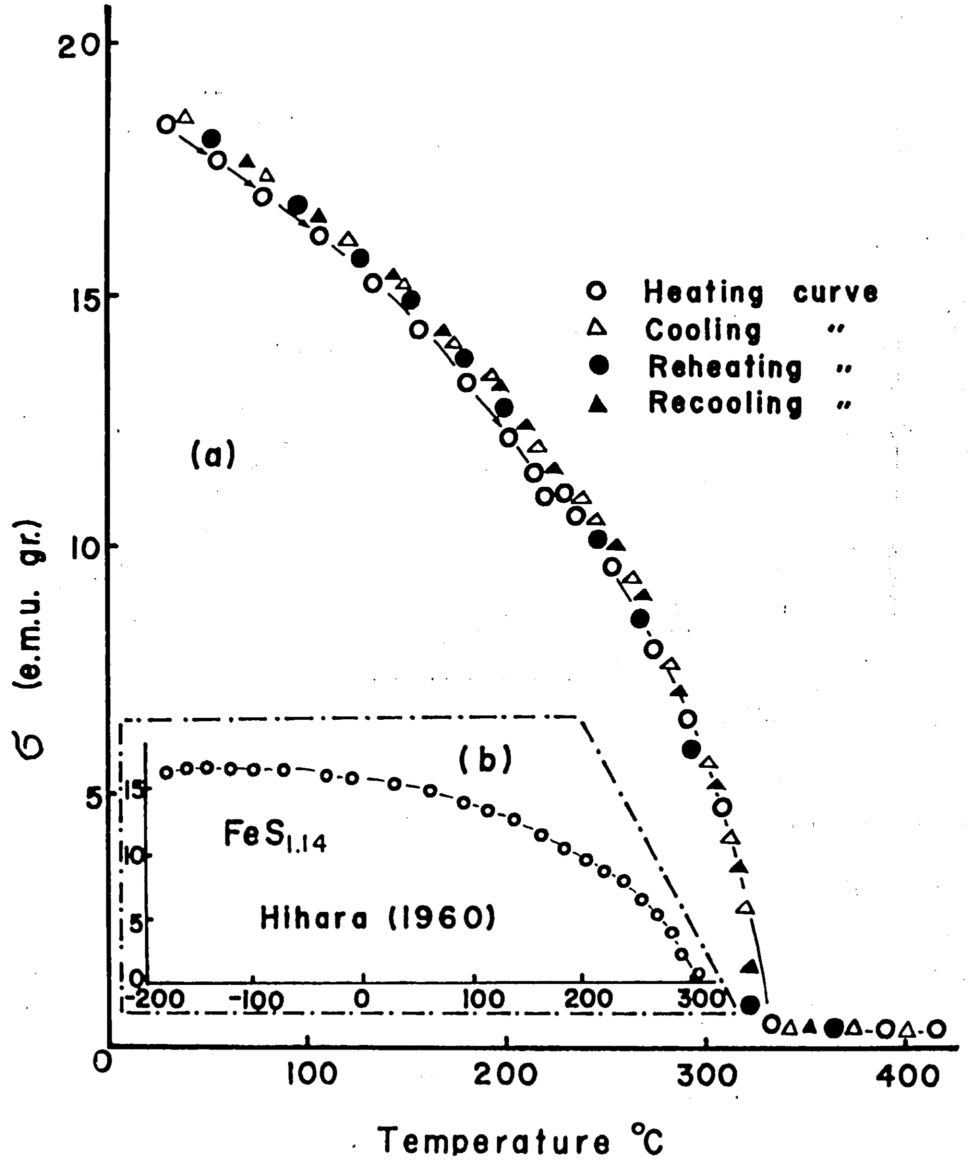

FIG. 13. Magnetization of natural pyrrhotite (Kawayama mine, 180-14) (a) and synthetic $FeS_{1.14}$ (b) as a function of temperature (Type IV).

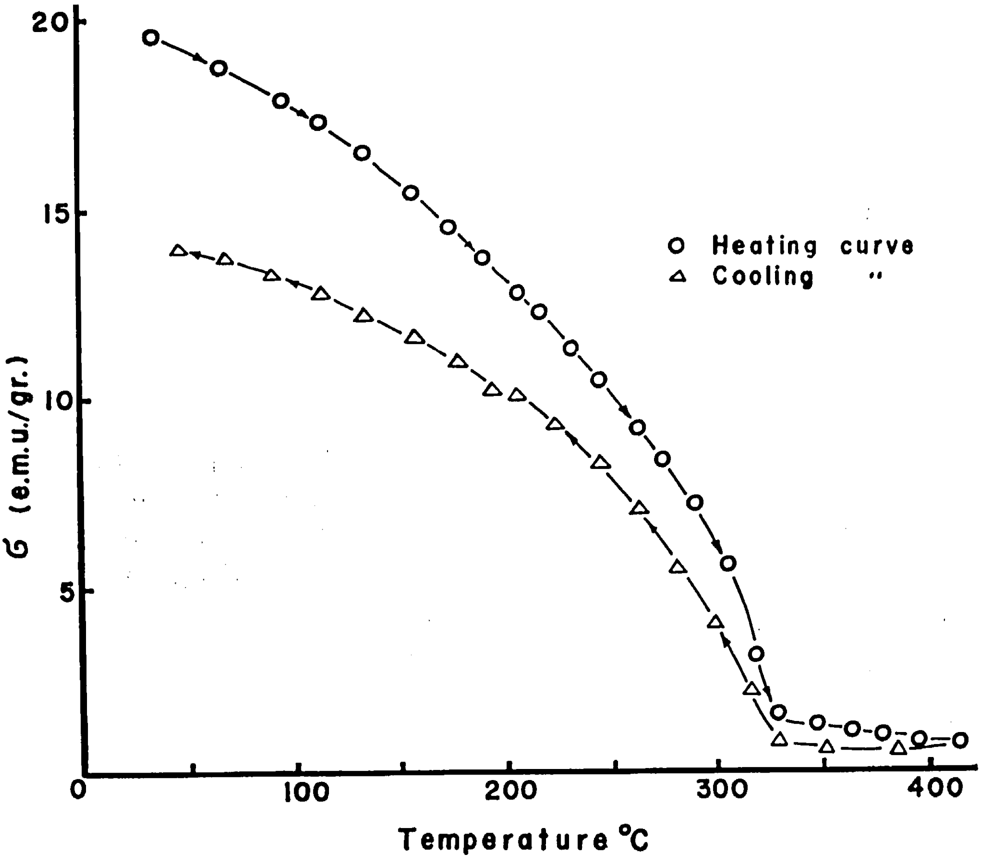

FIG. 14. Magnetization of natural pyrrhotite (Nonowaki mine) as a function of temperature (Type IV).

with σs are to be scrutinized.

1. x ≲ 1.09

In this range of sulfur content, determination of x is very difficult only from σs. Examination of σ-T curves is also so, in the case of natural FeS_x with x of far larger than 1.07, as have been pointed out by ARNOLD and REICHEN (1962) and by CARPENTER and DESBOROUGH (1964), since in the range of 1.06 ≲ x ≲ 1.09 no knicks related to α- and γ-transformations are confirmable on σ-T curves, as are shown in FIGS. 6 and 7. Nevertheless, σ-T curves of $FeS_{1.09}$ or $FeS_{1.08}$ given by HIHARA (1960) show some resemblance to those of Type I at room termperature to T_β (325°C), and furthermore, the values of σ given by HIHARA are in a very close relation to the present data. Thus it may be concluded that the specimens of 210-16 (FIG. 6) is nearly of $FeS_{1.09}$ and that from Makimine (Fig. 7) of $FeS_{1.07}$ in composition.

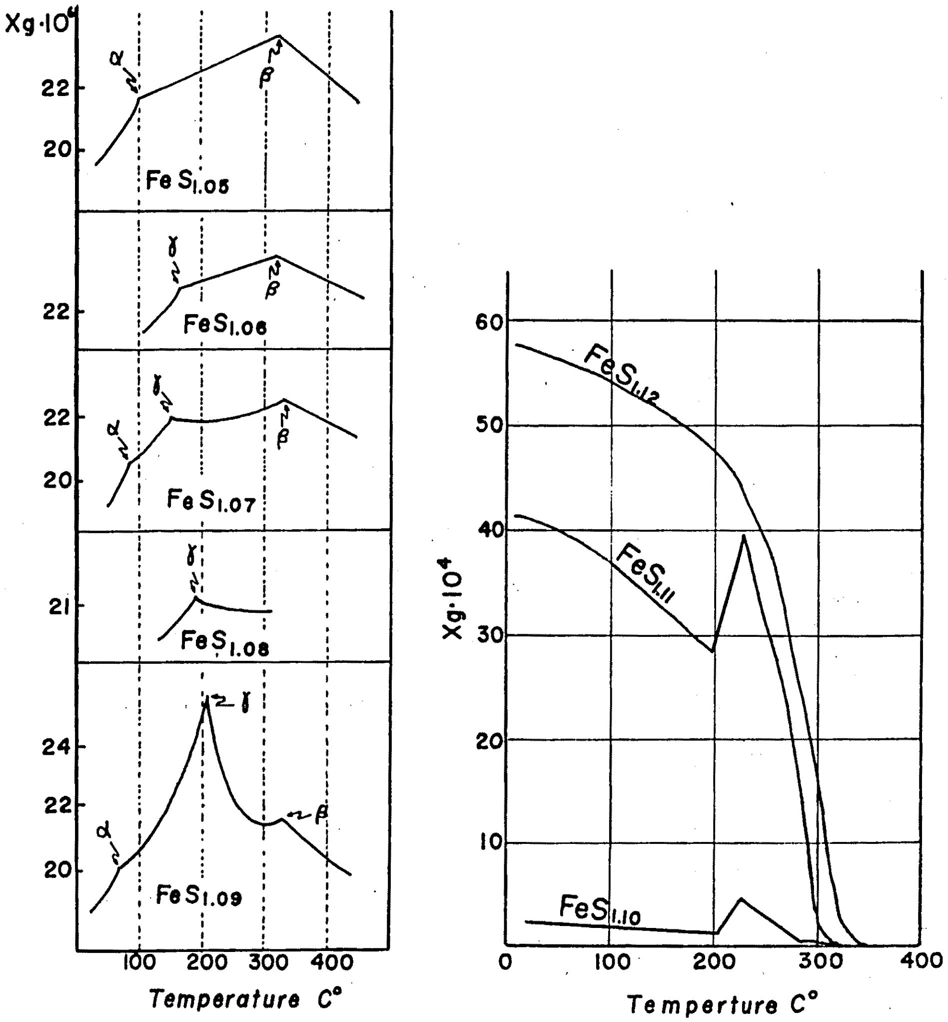

Fig. 15. Magnetization of synthetic FeS_x (after Haraldsen, 1941).

2. $1.09 \lesssim x \lesssim 1.11$

In this range, γ-transformation is conspicuous on all σ–T curves obtained through heating, cooling, reheating and recooling, as are shown in Figs. 8, 9 and 10. But it is considerably difficult to determine x only from the patterns of σ–T curves but inspection of T_{γ}, especially, T_{γ_2} or T_{γ_4} may be helpful for solving the problem in question. According to Haraldsen (1937, 1941) investigating FeS_x ($1.00 \leqq x < 2$) röntgenographically with variation of temperature, T_{γ} shifts regularly toward higher-temperature side with increasing S content. This relation together with the magnetical data of HIHARA (1960) and the D. T. A. data for synthetic FeS_x of SUGAKI and SHIMA (1965) are collected in FIG. 16. Since those three data are in good agreement with one another, the sulfur content x is derivable imediately from T_γ determined on σ–T curve.

On the other hand, T_γ is variable even for one specimen in the cases of heating (T_{γ_1}), cooling (T_{γ_2}), reheating (T_{γ_3}) and recooling (T_{γ_4}). In general, T_{γ_1} and T_{γ_3} almost coincide with each other, and T_{γ_2} and T_{γ_4} do so too. For instance, the specimen 240–127 (FIG. 8) shows T_{γ_1} at 265°C, T_{γ_2} at 255°C, T_{γ_3} 265°C and T_{γ_4} at 254°C, respectively. In the literatures given by HARALDSEN (1941), LOTGERING (1956) and HIHARA (1960), the knicks on cooling curves are acceptable as T_γ corresponding to T_{γ_2} (or T_{γ_4}) in the present data.

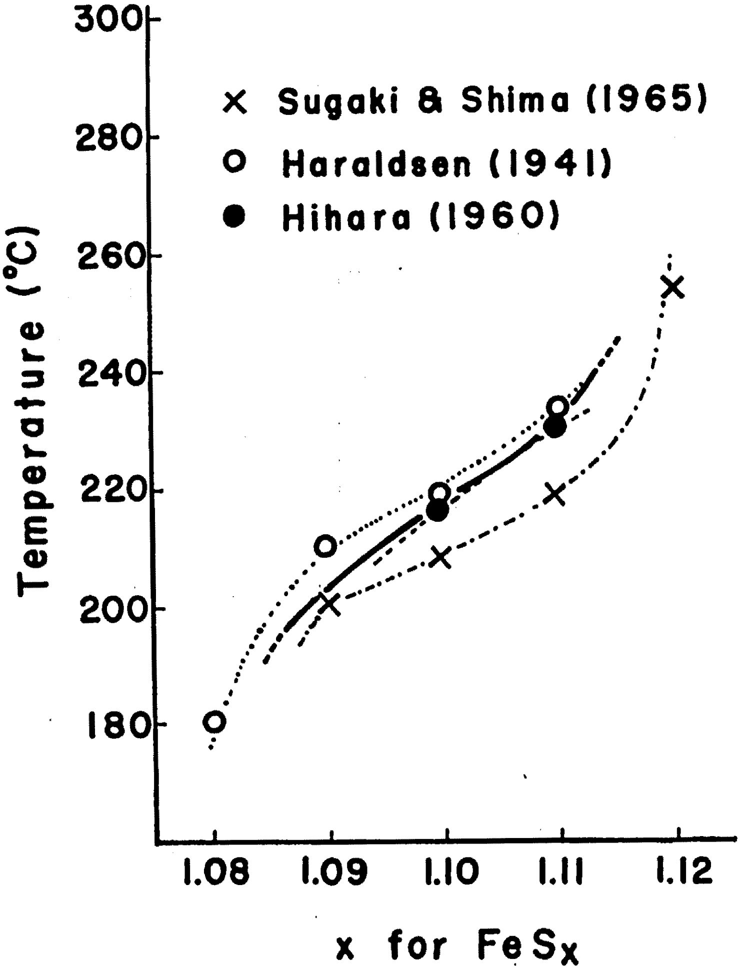

FIG. 16. Relation between T_γ and x for FeS_x (TAKENO *et al.*, 1966).

Under these circumstances, x has been determined from T_{γ} (T_{γ_2} or T_{γ_4}) on σ–T curves in FIG. 16, and the results, in general, agree well with those estimated from σs and d (102). For instance, T_{γ} for the Yanahara specimen (FIG. 9) appears at 204°C ($T_{\gamma_2}=T_{\gamma_4}=204$°C) and that for the Besshi specimen (FIG. 10) at 225°C ($T_{\gamma_2}=T_{\gamma_4}=$ 225°C). It hence results in that x amounts to 1.092 (47.801 atomic per cent Fe) in the former and to 1.104 (47.529 atomic per cent Fe) in the latter or, on the basis of d (102), to 1.098 (47.664 atomic per cent Fe) and to 1.107 (47.461 atomic per cent Fe) respectively.

3. $x \gtrsim 1.11$

In this range, the Types III and IV of σ–T curves are included. As for Type III with $1.11 \lesssim x \lesssim 1.13$, it is rather difficult to determine x owing to disappearance of

TABLE I. MAGNETIC PROPERTIES AND CHEMICAL COMPOSITIONS OF NATURAL PYRRHOTITE

Specimen No.	σ_s (e.m.u./gr.)	d (102) Å	Chemical composition		Magnetic type	Chemical composition by T_{γ} method
			x for FeSx	Fe atomic %		
Akagane - 1	0.7	2.0745	1.080	48.083	I	
〃 - 2	3.4	2.0713	1.093	47.782	II	$FeS_{1.091}$
Ohmine - 1	1.3	2.0742	1.082	48.034	I	
〃 - 2	5.9	2.0653	1.117	47.242	II	$FeS_{1.112}$
Kawayama 110-102	10.7	2.0645	1.120	47.175	III	
〃 110-106	20.1	2.0587	1.142	46.683	IV	
〃 110-109	14.8	2.0643	1.121	47.158	III	
〃 140-114	1.4	2.0745	1.080	48.083	I	
〃 140-129	13.7	2.0648	1.119	47.200	III	
〃 180-23	16.5	2.0619	1.130	46.950	IV	
〃 180-50	4.2	2.0695	1.100	47.617	II	$FeS_{1.097}$
〃 210-11	1.3	2.0721	1.090	47.850	I	
〃 210-53	13.0	2.0663	1.113	47.325	III	
〃 210-97	1.0	2.0767	1.070	48.300	I	
〃 240-124	20.5	2.0616	1.131	46.926	IV	
〃 240-126	8.3	2.0671	1.110	47.400	III	
〃 240-195	4.3	2.0703	1.097	47.683	II	$FeS_{1.095}$
Tsumo M - 4	19.7	2.0595	1.139	46.751	IV	
〃 M - 5	14.2	2.0673	1.109	47.417	III	
Nonowaki - 2	4.5	2.0682	1.105	47.500	II	$FeS_{1.103}$
〃 - 4	20.3	2.0611	1.133	46.883	IV	
Besshi - 3	2.2	2.0701	1.110	47.664	II	$FeS_{1.092}$
Makimine - 1	1.9	2.0767	1.070	48.300	I	
〃 - 3	5.3	2.0668	1.111	47.373	II	$FeS_{1.106}$
〃 - 5	18.3	2.0605	1.135	46.833	IV	
Yanahara - 1	17.2	2.0611	1.133	46.883	IV	
〃 - 2	2.1	2.0679	1.107	47.465	II	$FeS_{1.104}$
Outokumpu - 1	17.2	2.0673	1.109	47.417	III	

γ-transformation. The related knicks is to be pursued only on heating curve and not on T_{γ_2} or T_{γ_4}, so x cannot be evaluated by T_γ method mentioned above. Thus there is a room for estimation only from the σs. With respect to the Type IV without γ-transformation, on the other hand, it is surely confirmed that x is estimated about 1.13~1.14 in harmony with the value of σs.

V. RÖNTGENOMETRIC MEASUREMENTS

A. d (102) VALUES

Some typical data obtained for all specimens are listed in the Table I, from which their compositions are derivable. FIG. 17 shows the variation in composition determined by d (102) values of the specimens from the Kawayama mine. The maximum in frequency is in the range of $FeS_{1.105}$~$FeS_{1.115}$ or $Fe_{0.897}S$~$Fe_{0.905}S$ (47.506 ~47.281 atomic per cent Fe) and a submaximum is in the range of $FeS_{1.115}$~$FeS_{1.095}$ or $Fe_{0.897}S$~$Fe_{0.913}S$ (47.281~47.733 atomic per cent Fe).

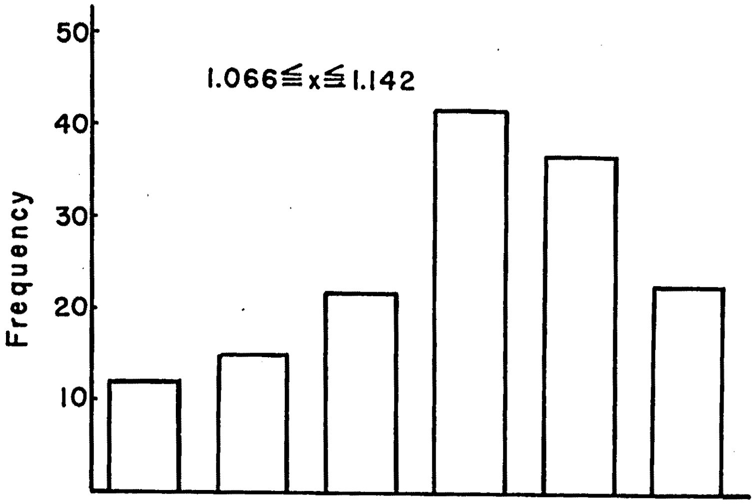

FIG. 17. Histogram showing the variation of the composition of natural pyrrhotite from the Kawayama mine.

The most excessive composition of sulfur is represented in the case of $FeS_{1.142}$ (240-104), a monoclinic form, while its minimum is in the case of $FeS_{1.066}$ (210-97).

The compositions of pyrrhotite from the ore deposits of some other types are almost similar to that from Kawayama being comprised within the limits determined for those of natural pyrrhotite from various localities by some authors such as ARNOLD and REICHEN (1962) ($FeS_{1.092}$~$FeS_{1.142}$), CARPENTER and DESBOROUGH (1964) ($FeS_{1.083}$~

$FeS_{1.510}$) and MUKAIYAMA and IZAWA (1965) ($FeS_{1.077}$～$FeS_{1.14}$).

B. TYPES OF THE (102) PATTERNS

The x-ray patterns for (102) spacing of hexagonal pyrrhotite in natural state are generally variable as was already pointed out by many investigators (HAYASE *et al.*, 1963 ; SUGAKI and SHIMA, 1965 ; MUKAIYAMA and IZAWA, 1965, etc.), whereas there are intimate relationships between their types and composition as well as magnetization. The patterns concerned are classified into the following six types (excepting the monoclinic form).

Type A with symmetrical and moderately sharp peak.
Type B with a small subpeak appearing in the lower part on the higher-angle side of the main peak.
Type C_1 with a subpeak in the upper part on the higher-angle side of the main peak.
Type C_2 with two peaks of intensity almost similar to each other.
Type D with some subpeaks, among which that of the lowest angle side is not the highest.
Type E with a considerably obscure peak.

FIG. 18 shows the frequency of these six types : that is, C_1 (30%), C_2 (23%), A (14 %), B (12%), D (11%) and E (10%) in order of abundance though with some obscuring in classification of the patterns, especially in the cases of C_1, C_2 and E exclusive of easier cases for A and B.

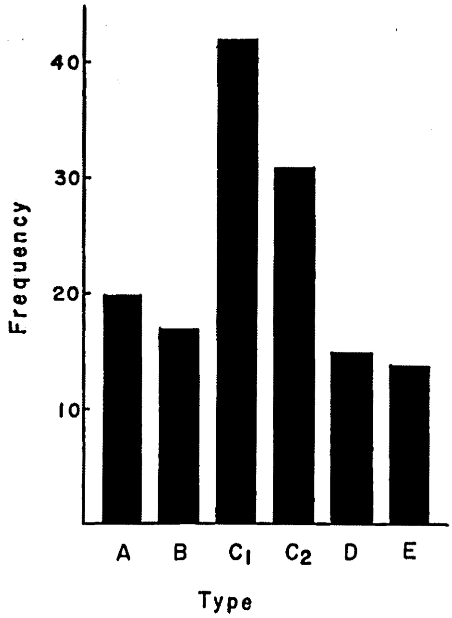

FIG. 18. Histogram showing the frequency of the six types.

These types are respectively correlated in composition and in σs, as are indicated in the following:

1. *Type A*

This type reveals the maximum frequency in the range from 2.068Å to 2.081Å corresponding to composition of $1.105 > x \geqq 1.095$ (47.506~47.733 atomic per cent Fe), as is shown in FIG. 19 and the submaximum in the range of more than 2.071Å. 90% of this type is concentrated in the range from 2.068Å to 2.072Å. Pyrrhotite of this type with little deficiency of iron is $FeS_{1.09}$ (47.847 atomic per cent Fe).

On the other hand, FIG. 20 shows the mutual relation between σs and the mode of (102) reflection. Type A is concentrated in the range of small values for σs ($1 \lesssim \sigma s \lesssim 4$).

It thus results in that the type A represents the pyrrhotite with composition of about $FeS_{1.095}$ (47.733 atomic per cent Fe), less deficiency of iron, and small value of magnetization, probably pointing to its stability in the structure.

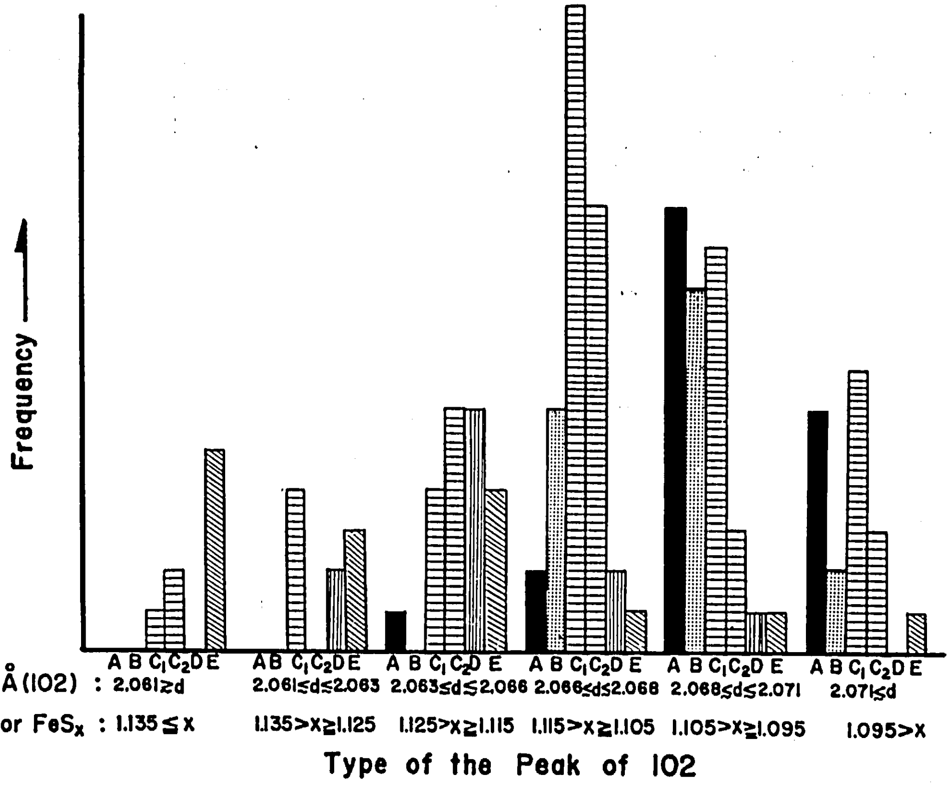

FIG. 19. Histogram showing the relation of frequency of the six types to the ranges of d (102) (Å) and x.

2. *Type B*

This type shows some trend similar to that of the type A but difference in that the submaximum is in the range of $1.115 > x \geqq 1.105$ (47.281∼47.506 atomic per cent Fe).

σs of this type is considerably variable in the range of $1 \lesssim \sigma s \lesssim 16.5$ and its concentration, though rather weak, is recognized in the range of $11.5 \lesssim \sigma s \lesssim 13.5$ (40%) while an homogeneous distribution is observable in the range of $\sigma s \lesssim 8.5$.

It is a conclusion that this type may represent the pyrrhotite with composition of approximately $FeS_{1.105}$ (47.506 atomic per cent Fe) and with iron deficiency more than that in the case of the type A, and σs of this type is rather variable in the range of $\sigma s \lesssim 15$.

3. *Type C_1 and Type C_2*

Type C_1 is of the most frequency (30%), ranging in $1.115 > x \geqq 1.105$ (47.281∼47.506 atomic per cent Fe), with iron deficiency more than those of the types A and B, but its patterns are found distributing throughout the limit of iron deficiency.

Type C_2 follows the type C_1 in frequency and bears a tendency in the sulfur content $x \lesssim 1.125$ (47.059 atomic per cent Fe) higher than in the latter type.

Type C_1 exhibits a very homogeneous distribution without any anomalies from 0 to 21 e.m.u./gr. in σs, while type C_2 is rather variable and recognized not in the middle part of $6.5 < \sigma s < 10.5$ but equally on both sides of these values.

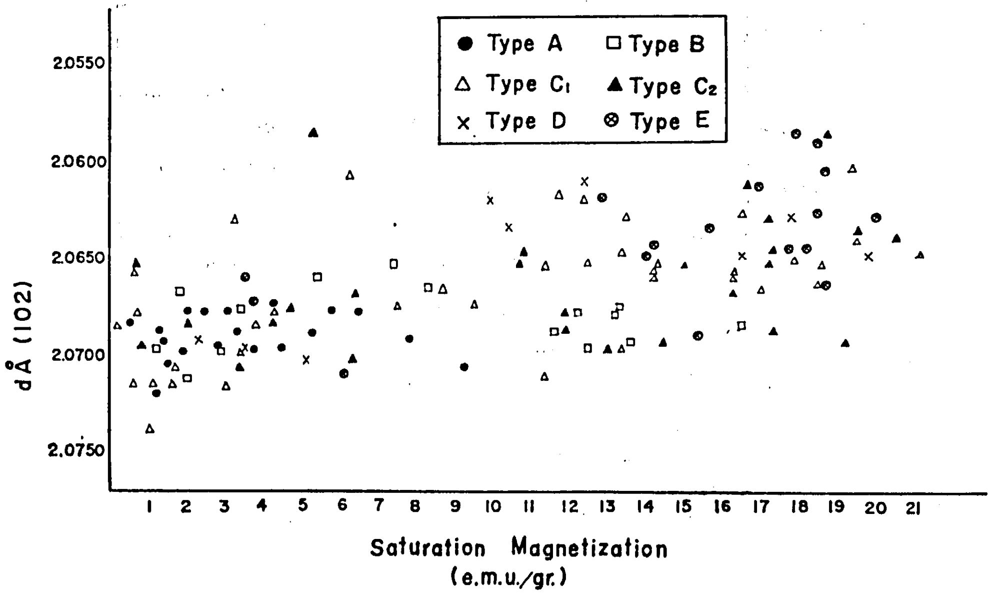

FIG. 20. Relation between σs and the type of (102) reflection of natural pyrrhotite.

4. *Type D and Type E*

In general, (102) pattern of hexagonal pyrrhotite becomes more complex with increasing deficiency in iron. These two types are of the most complex patterns among the other types.

Type D displays the most frequency in the range of $1.125 > x \geqq 1.115$ (47.059∼47.281 atomic per cent Fe) and an inclination showing iron deficiency more than those in the preceding four types. This type has apparently no concentration in σs similar to in the cases of the types C_1 and C_2.

Type E has a maximum frequency in the region with the most deficiency in iron, $x \geqq 1.135$ (46.838 atomic per cent Fe). This type is in the σs range higher than in the cases of other types (see FIG. 20).

C. THE X-RAY DISCRIMINATION CURVE

In spite of no chemical analyses for the present specimens, their compositions derived through magnetization method (especially by σ–T curves) are considered to

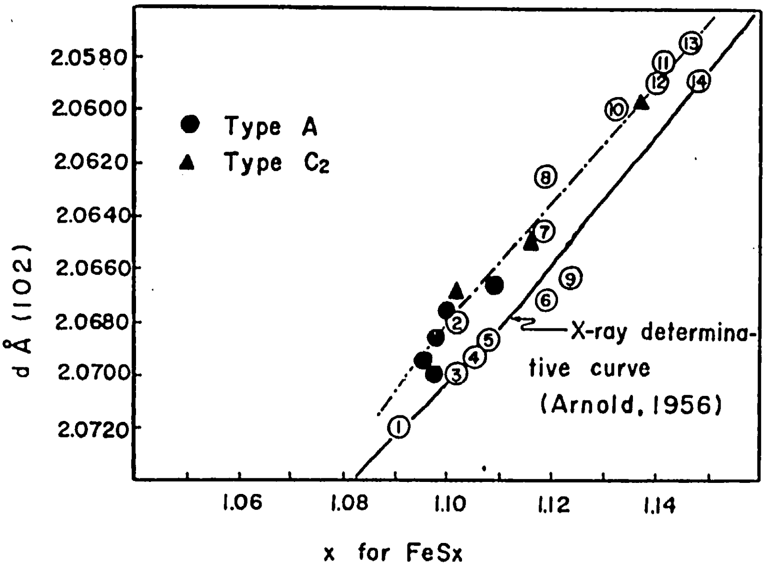

FIG. 21. Relation of composition to d (102) for natural pyrrhotite (TAKENO *et al.*, 1966).

Specimens from:

1. McAfee, N. J., 2. Bergbau, Austria,
3. Moise River, Quebec, 4. Toncray, Virginia,
5. Hybla, Ontario, 6. Bluebell, B. C.,
7. Highland Surprise, Idaho, 8. Treteca, Yugoslavia,
9. Funter Bay, Alaska, 10. Highland Surprise, Idaho,
11. Riondell, B. C., 12. Clearwater Brook, N. B.,
13. Highland Surprise, Idaho, 14. Kisbanya, Romania.

(ARNOLD and REICHEN, 1962).

have been accurate by determind if the impurities included be of non-ferrimagnetic ones. Under microscope, the impurities, usually less than 3 per cent in volume, are composed of quartz and calcite negligible for magnetization.

Fig. 21 shows the relation of composition to d (102) in the case of natural pyrrhotite. The compositions represented by black circles (Type A) and by triangles (Type C_2) are determined on σ–T curve through T_γ method, while the numbered points are taken from the data obtained chemically by Arnold and Reichen (1962). Arrangement of 22 points (including the present data) is generally in good agreement with the determinative curve. The fact is that the present data are less fractionated from the curve than those of 2, 8, 10, 11, 13, 12 and 17 given by Arnold and Reichen and regularly distributed along the Arnold's curve in the lower-deficiency area of iron, suggesting the presence of another curve running nearly parallel to the former.

The latter obtained from the present experiments can be given by equation:

$$Y = -0.225 + 2.315\,x\ (1.06 \lesssim x \lesssim 1.14)$$

$$(48.54 \sim 46.73 \text{ atomic per cent Fe}),$$

where x is the sulfur content in FeS_x and Y represents d (102) in Å (cf. Fig. 21). In contrast to this, the curve proposed by Arnold is expressed as:

$$Y = -0.0182 + 0.0767X - 0.00069X^2,$$

where Y is the same as that in the former equation and X implies the metal content expressed in atomic per cent. The curve derived from the latter equation by substituting X with x is almost parallel to the former, as is shown in Fig. 21.

At any rate, it seems somewhat problematical to determine the d (102) values of the types C_1, C_2, D and E röntgenometrically because of their obscure and non-symmetrical patterns. But as for the type A indicating moderately sharp reflections, represented by the blak circles in Fig. 21, there seems no room of doubt for determining the d (102) values though in the area of less defficiency in iron.

The discrepancy in two kinds of curves may be ascribed mainly to γ-transformation resulted from a certain regular arrangements of the iron vacancy. Thus, natural pyrrhotite with more impurities than those in the synthetic mineral, on cooling process, may cause the regular arrangement of the Fe vacancy at the temperature rather higher than that in the cases of synthetic mineral. Therefore, in the cases of composition similar to each other, T_γ of the natural pyrrhotite is to be higher than that of the synthetic one on cooling process.

D. X-RAY DIFFRACTION DATA

Some typical data of the natural pyrrhotite from the Kawayama mine are given in tables II and III. In table II, seven data for d (102) hexagonal pyrrhotite are listed, which are 2.0767, 2.0745, 2.0721, 2.0695, 2.0671, 2.0645 and 2.0619 in Å corresponding to the chemical composition of $FeS_{1.07}$, $FeS_{1.08}$, $FeS_{1.09}$, $FeS_{1.10}$, $FeS_{1.11}$, $FeS_{1.12}$ and $FeS_{1.13}$ (48.309, 48.077, 47.847, 47.619, 47.393, 47.170 and 46.948 atomic per cent Fe) respectively with reference to those of given by Berry and

TABLE II. THE DATA OF X-RAY POWDER DIFFRACTION FOR NATURAL HEXAGONAL PYRRHOTITE FROM THE KAWAYAMA MINE

(1)			(2)		210-97		140-114		210-11		180-50		240-126		110-102		180-23	
dÅ	I	hkl	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
3.45	5																	
3.00	40	100	2.97	33	3.01	44	2.99	33	2.98	35	2.97	45	2.98	40	2.97	45	2.97	30
2.87	5	002	2.88	4	2.88	5	2.89	6	2.88	5	2.88	8	2.87	10	2.88	10	2.87	8
2.65	60	101	2.65	33	2.65	54	2.65	55	2.65	60	2.64	50	2.65	50	2.64	55	2.63	50
2.08	100	102	2.06	100	2.077	100	2.075	100	2.072	100	2.070	100	2.067	100	2.065	100	2.062	100
1.728	50	110	1.71	33	1.725	34	1.725	30	1.725	40	1.718	32	1.720	30	1.715	35	1.712	37
1.617	20	103	1.61	7	—	—	1.616	5	—	—	—	—	—	—	1.609	5	—	—
1.496	5	200	1.48	4	—	—	—	—	—	—	—	—	—	—	—	—	1.485	3
1.452	10	201	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1.438	20	004	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1.328	40	202	1.32	13	1.327	4	—	—	—	—	1.323	3	—	—	—	—	1.319	2
1.298	10	104	1.30	5	—	—	—	—	—	—	—	—	—	—	—	—	—	—
					d (102) = 2.0767 $FeS_{1.07}$ $\sigma_s = 1.0$		d (102) = 2.0745 $FeS_{1.08}$ $\sigma_s = 1.4$		d (102) = 2.0721 $FeS_{1.09}$ $\sigma_s = 1.3$		d (102) = 2.0695 $FeS_{1.10}$ $\sigma_s = 4.2$		d (102) = 2.0671 $FeS_{1.11}$ $\sigma_s = 8.3$		d (102) = 2.0645 $FeS_{1.12}$ $\sigma_s = 10.7$		d (102) = 2.0619 $FeS_{1.13}$ $\sigma_s = 16.5$	

(1) Natural pyrrhotite,
(by BERRY & THOMPSON, 1962)
(2) Natural pyrrhotite,
(ASTM, 1-1247)

TABLE III. THE DATA OF X-RAY POWDER DIFFRACTION FOR MONOCLINIC PYRRHOTITE

(1)			(2)		110-106		240-104	
d (obs) Å	I	hkl	dÅ	I	dÅ	I	dÅ	I
5.74	mw	111, $\bar{1}11$	5.78 5.76	12 10			5.78 5.72	10 10
5.27	w	112, $\bar{1}12$	5.27	10			5.28	12
4.71	w	113, $\bar{1}13$	4.70	10			4.70	12
4.43	vvw	211, $\bar{2}11$						
3.61	w	106, $\bar{1}06$ 115, $\bar{1}15$	3.63 3.62 3.60	8 8 8			3.63	3
3.43	w	020, 310	3.47	10				
3.22	vw	206, $\bar{2}06$ 116, $\bar{1}16$	3.22 3.20	15 12				
3.13	m	313, $\bar{3}13$ 023	3.15 3.13	5 5	3.15	5	3.14	7
2.975	s	400, 220	2.977	72	2.976	65	2.979	80
2.849	vw	008					2.857	10
2.634	vs	404, $\bar{4}04$ 224, $\bar{2}24$	2.645 2.639 2.634	78 60 55	2.640	70	2.645 2.635	50 70
2.547	vw	316, $\bar{3}16$ 026	2.550	8				
2.374	vvw	019			2.370	7		
2.205	vw	422, $\bar{4}22$ 132, $\bar{1}32$			2.195	5		
2.159	vw	133, $\bar{1}33$			2.142	5		
2.057	vvs	408, $\bar{4}08$ 228, $\bar{2}28$	2.065 2.062 2.056 2.049	100 100 78 30	2.058 2.053	95 100	2.065 2.057	100 95
1.982	vvw	331, $\bar{3}31$						
1.766	w	428, $\bar{4}28$						
1.718	s	040 620	1.719	56	1.716	20	1.719	40
1.633	w	242, $\bar{2}42$	1.635 1.631	5 5	1.630 1.628	10 10		
1.488	vw	800 440						
1.439	w	804, $\bar{8}04$ 444, $\bar{4}44$	1.443 1.439	10 10	1.486 1.476	15 15	1.440	7
1.425	w	0.0.16	1.426	10			1.423	10
1.323	mw	808 448	1.324 1.321	15 15	1.319	30	1.323	10
1.315	mw	$\bar{4}48$ $\bar{8}08$	1.315	12	1.316	30	1.316	5
1.288	vw	4.0.16 2.2.16	1.289 1.286	7 7				

(1) X-ray powder data for natural monoclinic pyrrhotite by CARPENTER & DESBOROUGH (1964).

(2) X-ary powder data for monoclinic pyrrhotite synthesizd in 20% Na_2S solution (SUGAKI & SHIMA, 1965).

THOMPSON (1962) and ASTM (1-1247). The lattice constant $a = 3.452$ given by BERRY and THOMPSON is generally in good agreement with the present data especially in the composition range of $x \lesssim 1.09$.

On the other hand, the values of the d (102) for the mineral concerned decrease regularly from 2.0764Å for $FeS_{1.07}$ to 2.0619Å for $FeS_{1.13}$. Considering the fact that the lattice constant a shows no appreciable change, the lattice constant c contracts gradually with increasing sulfur content. The rough estimation based on the present data listed in table II demonstrates that the c contracts from 5.78Å (a=3.44Å) for $FeS_{1.07}$ (210-97) to 5.73Å (a = 3.43Å) for $FeS_{1.13}$ (180-23), where a are calculated from d (100).

Two data of the monoclinic pyrrhotite from the Kawayama mine are given in table III referring to those given by CARPENTER and DESBOROUGH and to that of the synthetic one by SUGAKI and SHIMA.

VI. APPLICATION TO THE ORE DEPOSIT

A. OUTLINE OF GEOLOGY AND THE ORE DEPOSIT

The geology distributed in the Kawayama district consists of the crystalline schists, a part of the Sangun-Motoyama metamorphic group, and of non-metamorphic Palaeozoic formation overlying conformably on the former. The upper group is composed of alternation of slate and sandstone, and the lower group, of graphite-schist accompanied with subordinate amount of green schist. The schist (mainly graphite-schist) in the lower group commonly shows a distinct schistosity, the planes of which are generally parallel to the bedding planes.

The ore deposit of the Kawayama mine is, in general, bedded in form nearly parallel to the schistosity planes of the country rocks consisting of the schist. The ore body is accustomed to reveal a general strike of N40°～50°E in the southern part and N30°～40°W in the northern part, with dip of 5°～20°W (see FIG. 22). Its thickness is about five meters on an average but variable in the range from a few centimeters to some dozen meters.

The specimens provided for the present experiment were mainly collected from the lower ore deposit (cf. TAKENO, 1963). The very deposit with a scale of 120m～150m along its strike-side and of some hundreds meters along its dip-side is confined to a unit of the ore body situating between the Higashi-dani fault and the Nishidani fault. As a whole the ore body bears a layered form in the cross sections traversing along the strike- and dip-sides, and there are however innumerable partings in the ore body as well as in the wall rock.

B. CHARACTERISTIC DISTRIBUTION OF σs

The values of σs are divided into those of four zones such as I: $\sigma s < 5$, II: $5 \leq \sigma s < 10$, III: $10 \leq \sigma s < 15$ and IV: $\sigma s \geq 15$. FIGS. 23, 24 and 25 show their horizontal distribution on each level at the lower ore deposit, indicating a zonal arrange-

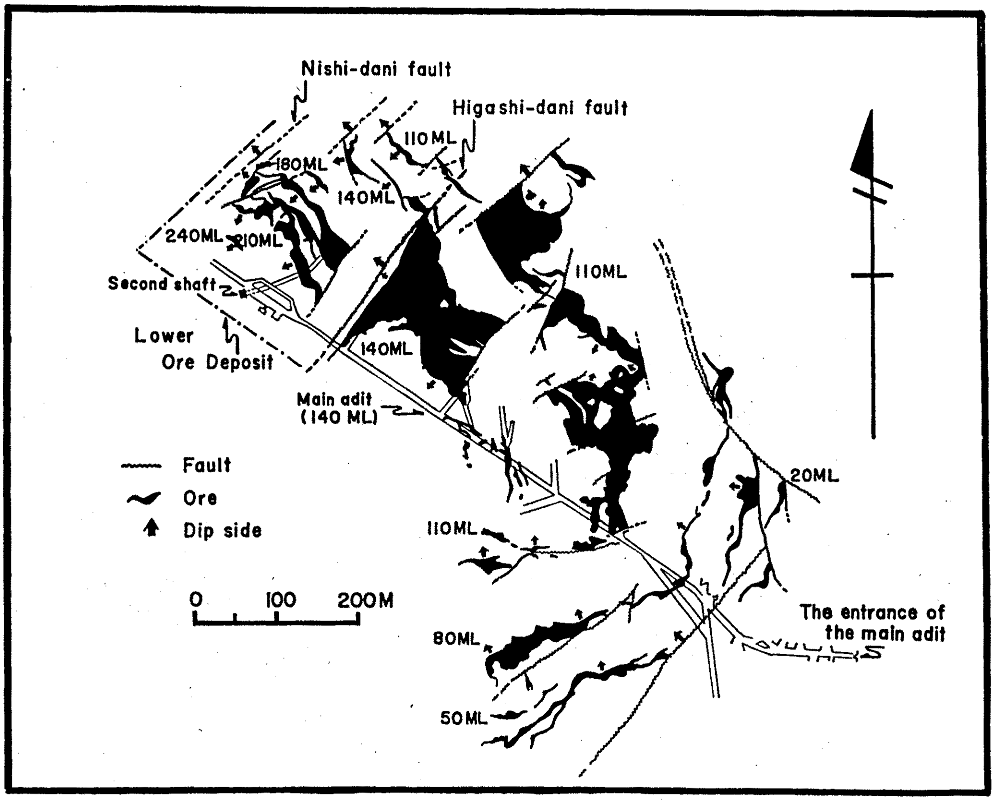

FIG. 22. Ore deposits of the Kawayama mine.

ment around a certain center, as are outlined in the follwing.

On the -180m level, the strongest IV zone is concentrated in the central part of the ore body surrounded by the III zone, in the outer part of which the II zone is developed partially. On this level, the zoning of σs, though rather incomplete, is characterized in such a tendency that the stronger is surrounded by the weaker. The weakest zone I is almost not confirmable on this level (see FIG. 23).

On the -210 m level, the central part of the ore body is occupied by the weakest zone exclusive of the northwestern part bearing the strongest zone similar to that on the just upper -180m level surrounded by the III zone. The central weakest zone is almost completely surrounded by the stronger II zone contrary to the arrangement on the -180m level, although in the northwestern part of this level the strongest zone IV is surrounded by the weaker zones III and II in order. This level situating just at the central part of the ore deposit is characterized by development of the weakest zone corresponding to that of the composition with low iron deficiency or rather stable composition of pyrrhotite (see FIG. 24).

On the other hand, on the lowermost -240m level excavated in thick limestone

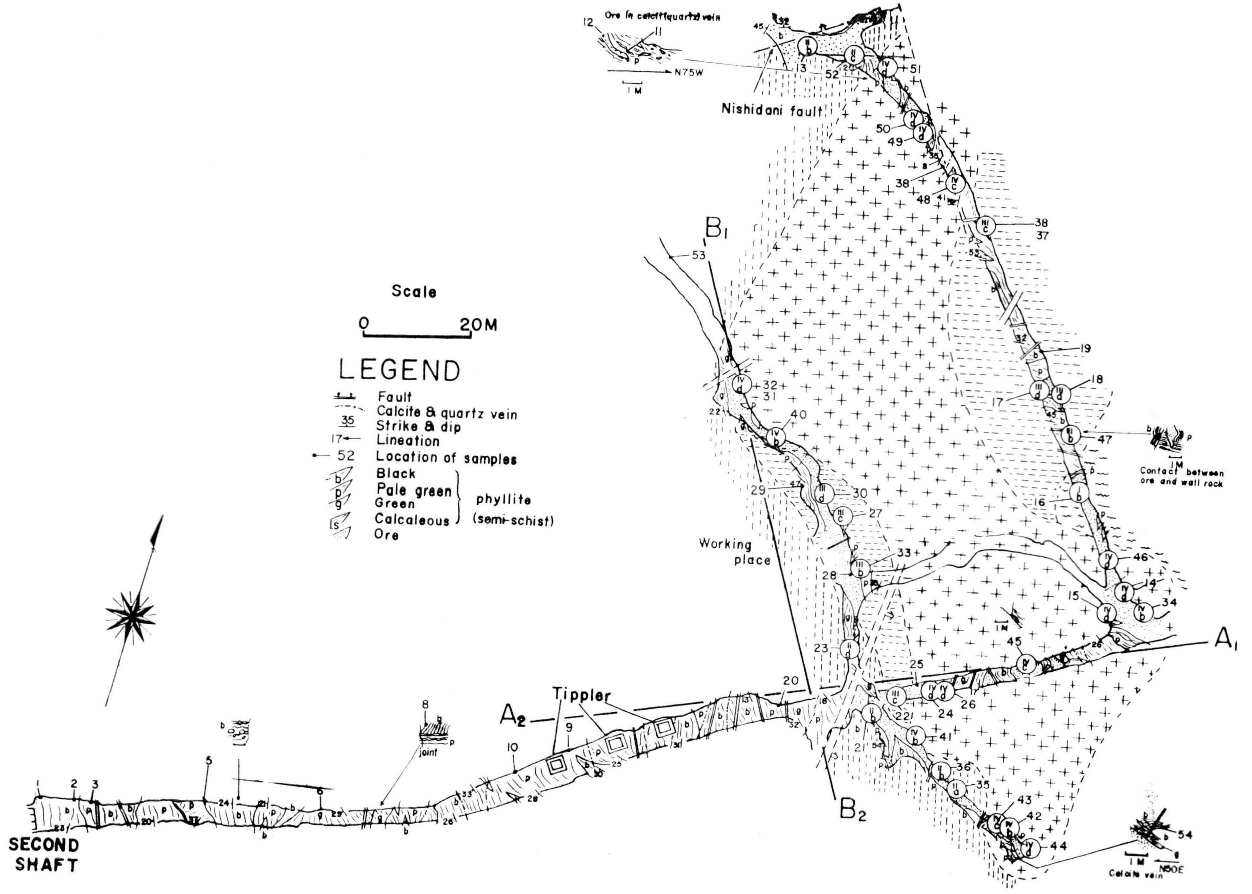

FIG. 23. Geological map of the -180m level with distribution of σs. Numbers in circles (I, II, III, IV) denote the four gradiations, i.e. I; $\sigma s < 5$, II; $5 \leqq \sigma s < 10$, III; $10 \leqq \sigma s < 15$, IV; $\sigma s \geqq 15$, and letters (a, b, c, d) denote the intervals of x, i.e. a; $x < 1.095$, b; $1.095 \leqq x < 1.11$, c; $1.11 \leqq x < 1.12$, d; $x \geqq 1.12$, respectively.

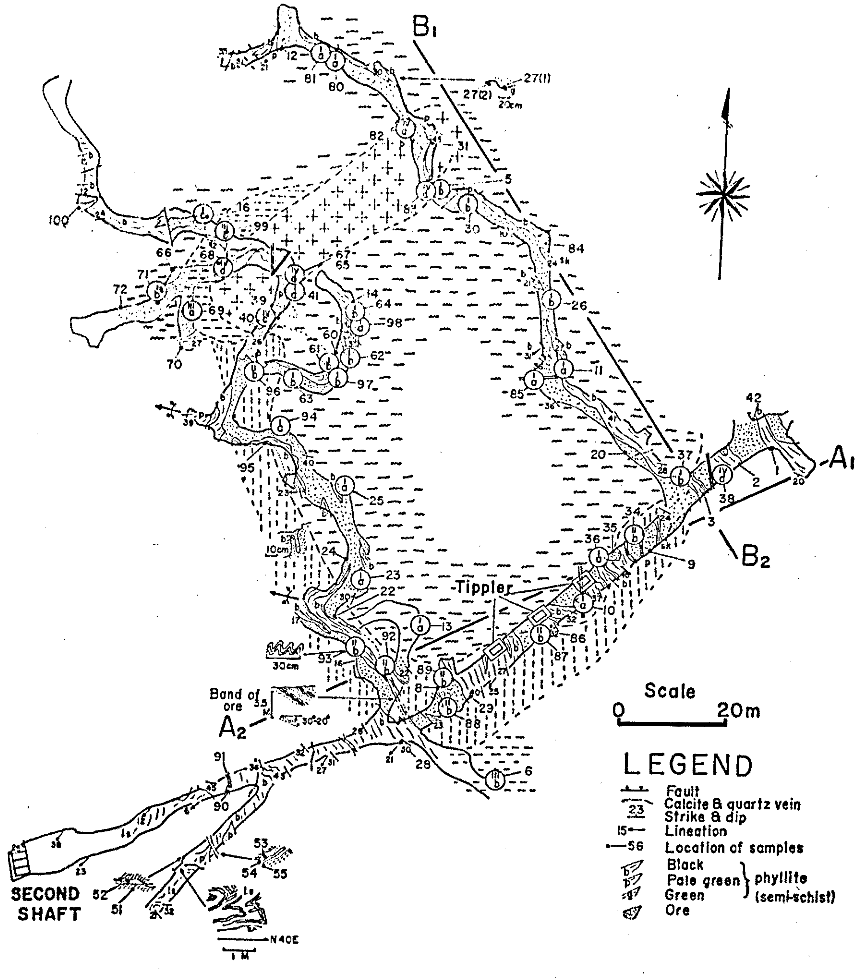

FIG. 24. Geological map of the -210m level with distribution of σs. The emblems are same as those shown in FIG. 23.

distribution of the σs values is also characteristically different from that on the upper two levels. The strongest zone appearing in the central to northwestern part is just combined with the extension of the strongest part of the upper two levels and surrounded regularly by the weaker zones III and II in order. The weakest zone I is not recognized on this level, where the ore body in question thins out in the calcaleous rocks (see FIG. 25).

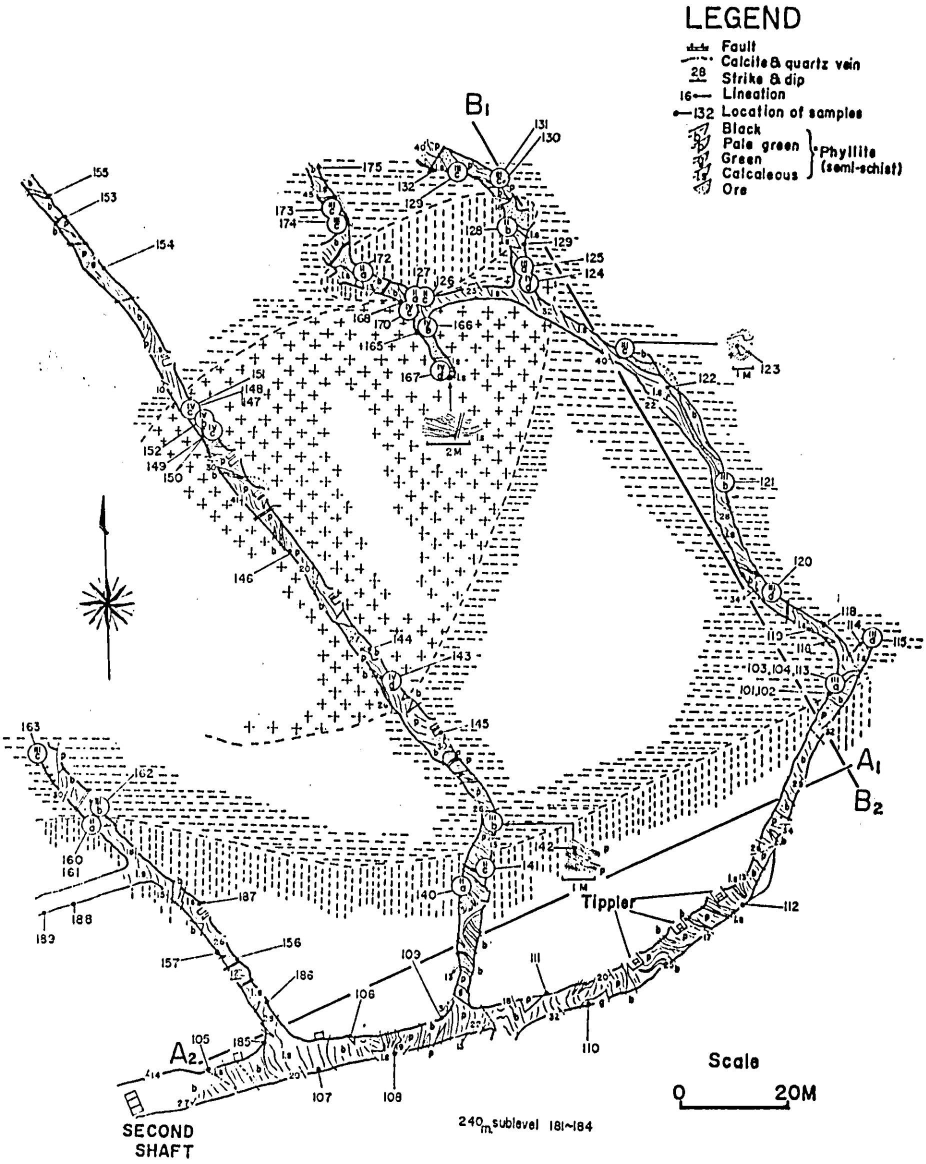

FIG. 25. Geological map of the -240m level with distribution of σs.

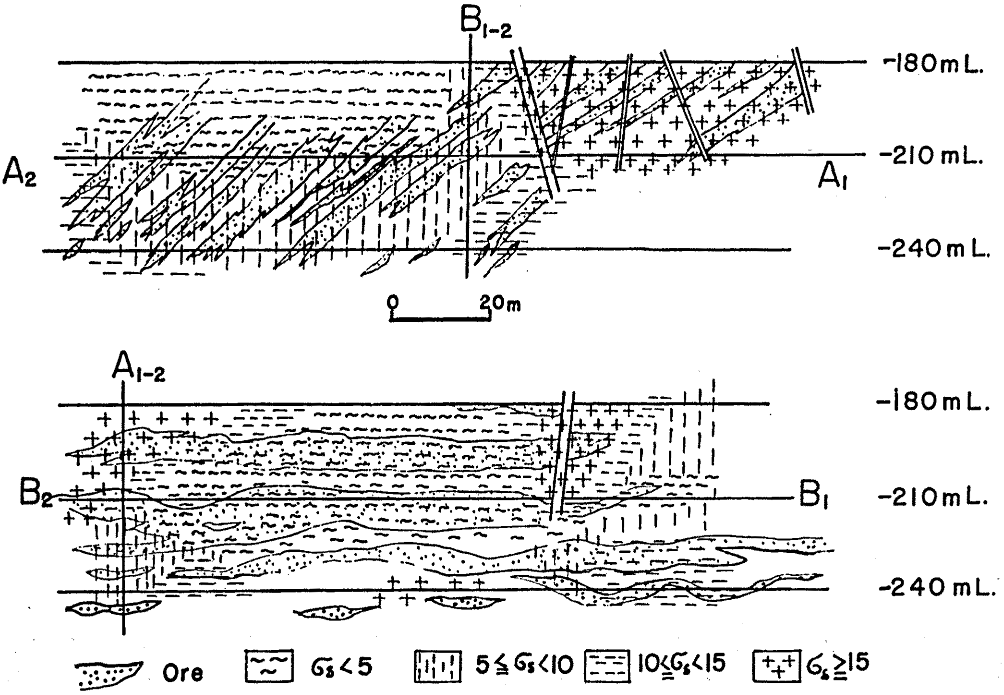

FIG. 26. Schematic profile sections of the lower ore deposit along $A_1 \sim A_2$ and $B_1 \sim B_2$ drawn in FIGS. 23, 24 and 25.

Furthermore, schematic profiles for some zonal distribution of σs are shown in FIG. 26. Generally, the central part of the ore deposit is in accord with the weakest zone surrounded the stronger, but the strongest shows rather irregular distribution, situating roughly in the outermost part of the ore deposit.

C. σS, COMPOSITION AND FORMATION TEMPERATURE

The saturation magnetization and the composition deduced from d (102) values are generally in good correspondence to each other, as are shown in FIGS. 23, 24 and 25, wherein the numbers I, II, III and IV denote the four zones stated in the preceding, and the letters a, b, c and d the intervals of x, i.e. a : $1.095 > x$, b : $1.11 > x \geqq 1.095$, c : $1.12 > x \geqq 1.11$, d : $1.12 \leqq x$, respectively. Combining the numbers with the letters in such forms as (I-a), (II-b), (III-c) and (IV-d), it seems clear that both modes of distribution well coincide with each other for 55 per cent of all specimens. Many other combinations such as (I-b), (I-c), (II-c), etc. are possible, among which incongruity is however generally small in the case of (I-b), (II-c), (III-b), (III-d), etc.

On the other hand, the "pyrrhotite-pyrite solvus" relation established by ARNOLD *et al.* (1962) and ARNOLD (1962) is questionable at the temperature above 600°C due to an uncertainty in temperature (±50°C), as was already pointed out by KULLERUD and YODER (1959), ARNOLD (1962) and recently by CARPENTER and DESBOROUGH (1964), for pursuing the genetical conditions of ore deposits.

Applying this to pyrrhotite from the Kawayama mine, the most specimens are to be included in the temperature range below about 340°C. The highest temperature suitable for formation of pyrrhotite is about 470°C (240–104) in correspondence to the strongest magnetization appearing in the IV zone and that for the specimens in the central part of the ore deposit is about 300°C.

It is however regrettable because of its restriction only within the domain of atomic per cent Fe $\lesssim$ 47.25 or in the range of $x \gtrsim 1.116$ that the relation is capablying only to a half of the present specimens.

VII. CONSIDERATIONS

The signification for the experimental results obtained above will hereunder be considered.

I. *Kawayama ore deposit*

Although there have been general views given for complicated magnetic behaviors of the iron sulfides, almost none has hitherto been alluded to in relation to geology. With all the data related to thermo-analytical, electrical and röntgenometrical studies, it appears that any satisfactory results have not so far been obtained owing to their complicated characters connected with remarkable variation in sulfur content and temperature. As has however been exhibited, the saturation magnetization of pyrrhotite from the ore deposit under consideration is not uniform in distribution but reveals some zonal arrangement suggesting heterogeneity in ore deposition. It can probably be concluded that the specimens collected from the central part of the ore deposit, even if not from the whole mass of the ore body, shows the weaker magnetization compared to those from the outer part. It is of course the case with the specimens collected from -140m level, the main adit of this mine. In other words, the central part of the ore body is composed of the pyrrhotite with less deficiency in iron content, than its outer part. This fact is reasonably acceptable because the central part might have been formed in such a condition as was more stable for the mineral than in the outer part.

It is furthermore supposed that the assumed ore fluid might have come from a certain horizon, descending downward along the dip-side. As is evident in FIG. 26, the part of the strongest magnetization is concentrated on -180 m level, where several faults are found developed here and there. The reality may be that σs of the mineral gradually decreases with depth of horizon. Thus the related ore deposit might have been formed by certain ore fluids derived from a certain level upper than -180m level to the lower levels in the schistosity plane of the country rocks and stagnant at least in the calcaleous rocks developed predominantly on -240m level.

The results mentioned above probably give a solution for origin of the deposit developed almost concordantly with the wall rocks.

In Japan there are many deposit known as 'Kieslager', which are characterized with their occurrence in slightly or remarkably metamorphosed rocks as well as their concordance with the main structures of wall rocks and composed chiefly of cupriferous iron sulfides. Although these ore deposits are believed to be genetically not always in connection with those of the same origin, the leading opinions given by some authors (cf. KOJIMA and co-workers, 1956) from petrological and stratigraphical point of view are those combining their genesis with the materials deposited in relation to submarine eruption in the original geosyncline.

As to origin of the Kawayama ore deposit, previous works have been based on its occurrence in the sheared or fractured zone assumed to appear in connection with the so-called Kitayama thrust named by KOJIMA (1950, 1953). Subsequently some studies made by TAKASHIMA and TOMITA (1951), NOMURA and HONDA (1952) and GOHARA (1955) have supported KOJIMA's view to more or less extent.

On the other hand, MITSUNO (1960) published an opinion of grouping this kind of ore deposits into a type of Kieslager only on the basis of its occurrence. This however seems too low in grade to give a clue to such a classification even for the reason of parallelism of the structure of wall rocks with those of the ore minerals recognized in the deposit under consideration. The zonal or oriented distribution of σs of pyrrhotite from the ore deposit concerned suggests that the special situation or apparent structural relation between the wall rocks and the ore bodies as well as no correlation between σs of pyrrhotite and its paragenesis give little or another meaning in investigation of the ore deposit.

II. *Magnetic properties of natural pyrrhotite*

a) As was seen from the measurements of the saturation magnetization and that of the magnetization as a function of temperature, the magnetic properties of pyrrhotite depends very sensibly on its chemical composition. Therefore it is possible to presume with high accuracy the chemical composition of pyrrhotite from the state of magnetization. It should be noted, however, that, as was stated already, this mineral indicates crystallographically α- and β-transformations and magnetically α-, β- and γ-transformations together with complicated behaviors under heating or annealing process or similar condition. Furthermore, as a result of the fact that pyrrhotite is a sort of 'berthollide compound', it is also to be remembered that even its synthetic specimen has a tendency bringing on heterogeneity. Naturally, this appears considerable in the case of natural specimen, and an irreversibility is discernible in magnetization as a function of temperature in association with more complicated circumstances. This heterogeneous property can be removed fairly well through heating above 450°C in vacuo probably as a result of sulfur diffusion. Hence, in classifying the specimens into the four types based on the σs values, this heterogeneity is to be preliminarily removed with repetion of heating and cooling. In addition to this, the mineral shows strong anisotropism in composition ($\sim FeS_{1.14}$) with ferrimagnetism because of easier direction of magnetization (spin arrangement) lying in c-plane. Hence, after removal of this strong anisotropy the measurement should be performed by using pure polycrystalline or powder specimens. Especially in the case of specimens belonging to the Type II with γ-transformation, σs at the room temperature is not determined uniquely, as are seen in Figs. 8, 9 and 10. This comes from the fact that transformation of the regular-irregular arrangement of Fe-vacancy strongly depends on the heating process, causing a difficulty in clarifying mechanism of the γ-transformation.

Table IV. A Classification of Natural Pyrrhotite Based on the Magnetic Properties.

Magnetic Type	Definition	Saturation Magnetization σ_s (e.m.u./gr.)	Chemical Composition x for FeS_x	Remarks
Type I	With no α- and γ-transformations above the room temperature	$\sigma_s \lesssim 1$	$1.05 \lesssim x \lesssim 1.09$	Although the γ-transformation is appeared slightly at 150°C when $x = 1.07$, the Δ type magnetization is not recognized.
Type II	With well defined γ-transformation	$1 \lesssim \sigma_s \lesssim 6$	$1.09 \lesssim x \lesssim 1.11$	The γ-transformation temperature changes regularly between 190°C and 250°C according to x.
Type III	With γ-transformation superposed on the σ-T curve of Weiss type	$6 \lesssim \sigma_s \lesssim 15$	$1.11 \lesssim x \lesssim 1.13$	This type corresponds to "Mixed type" and the x may represent the average value of the mixture.
Type IV	Showing σ-T curve of Weiss type	$\sigma_s \gtrsim 15$	$x \gtrsim 1.13$	Specimen of complete Weiss type is rare, because of the property of mixture.

In the present experiment, oxidation of the mineral have little been taken into account, since the measurements have been carried out for the specimens sealed in the silica tubes evacuated down to about 10^{-6}mm Hg. Pyrrhotite, however, is strongly oxidized even in the air at room temperature. Thus, the heat treatments in the air get to bring on alteration or oxidation, resulting in irreversibility of the results. Inasmuch as the similar processes before sealing in the evacuated tubes are necessarily unavoidable, the σ-T curves obtained (Figs. 6 and 7) are surely influenced by possible oxidation on the surface of the specimen as much as by heterogeneity of the natural pyrrhotite.

The fact that the formation of magnetite is röntgenographically and magnetically not observed in the case of very weak oxidation is probably attributable to that oxygen ions occupying the lattice points of sulfur ions behave like the latter.

b) Essential mechanism of ferrimagnetism in pyrrhotite was explained by Bertaut (1954). According to his view, there are alterations of the sublattices with and without vacancies in the structure of $FeS_{1.14}$ (Fe_7S_8), ferrimagnetism is considered to take place when the numbers of Fe^{3+} included in these two kinds of sublattice become different from each other, and the experimental data obtained for $FeS_{1.14}$ (46.73 atomic per cent Fe) with about $0.25\mu_B$ of spontaneous magnetization per molecule can be conveniently interpreted if Fe^{3+} ions are comprised only in the sublattice with vacancy (B-layer). From his theory the saturation magnetization can be estimated 17.3 C.G.S.e.m.u./gr. at 0°K and less than 17 C.G.S.e.m.e./gr. at the room temperature. However, its value obtained in the present measurement amounts to 21.2 C.G.S.e.m.u./gr. and that given by HAYASE *et al.* (1963) is also larger. These facts may point to presence of Fe^{3+} not only in the B-layer but also in the A-layer without vacancy.

On the other hand, these values are fairly small compared with 34 and 36 C.G.S. e.m.u./gr. given by BERTAUT for respective cases with Fe^{3+} present only in the B-layer ($2\delta\mu_B$) and with that present at random in the A- and B-layers. Consequently, in the specimen with 21.2 at maximum in σs at the room temperature, 89 per cent of Fe^{3+} are considered to be located in the B-layer.

III. d (102) *and its reflection*

The x-ray determinative curve is applicable to the hexagonal pyrrhotite with iron deficiency for scrutinizing similarity in relation between the (102) spacings and composition for the natural and synthetic specimens.

Since the works shown by ARNOLD (1956) and ARNOLD and REICHEN (1962), many investigations have been concerned with the x-ray method for determining the composition and the formation temperature of pyrrhotite from some types of the ore deposits. For instance, the origin of magnetite and pyrrhotite assemblage at the Yanahara mine, Japan have been genetically studied by TSUSUE (1962), formation process of pyrrhotite-sphalerite ores at the Highland-Surprise mine, Idaho by ARNOLD *et al.* (1962) and origin of the pyrrhotite-arsenopyrite ores at the Ylöjärvi deposit, Finland by CLARK (1964). In all of these result, compositions of natural pyrrhotite group are restricted to those representing three ranges, *i.e.* 1) troilite phase ranging from about $FeS_{0.992}$ to $FeS_{1.008}$ (50.20~49.80 atmic per cent Fe), 2) hexagonal phase ranging from about $FeS_{1.06}$ to $FeS_{1.37}$ (48.55~46.80 atomic per cent Fe) and 3) monoclinic phase ranging from about $FeS_{1.128}$ to $FeS_{1.151}$ (47.00~46.50 atmic per cent Fe).

MUKAIYAMA and IZAWA (1965) pointed out that in natural pyrrhotite group five stable phases exist, *i.e.* 1) troilite with d (102) of 2.093Å and 2) hexagonal pyrrhotite with d (102) of 2.074Å, 3) that with 2.070Å, 4) that with 2.066Å, and 5) monoclinic pyrrhotite. Moreover they emphasized that each phase of pyrrhotite can be distinguished on the basis of its d (102) as well as optical and magnetic properties. Although their conclusions are not in agreement with the present results with respect to continuity of the solid solution of hexagonal pyrrhotite, their excellent photographs as to intergrowths of exsolution lamellae of natural pyrrhotites are rich in suggestion for further study of the problem concerning the solid solution or stability relation of natural pyrrhoties.

Compositions of the specimens from the Kawayama mine are in the range from $FeS_{1.066}$ to $FeS_{1.142}$ and troilite phase is not detectable by means of x-ray and under reflection microscope. In regard to this fact, the report brought to light by Clark (1964, 1966) on the lamellar intergrowth of troilite and intermediate pyrrhotite (Grønvold and Haraldsen, 1952) at the Ylöjärvi deposit, Finland is surely noteworthy and contributes to avoid confusion in the Fe-S system with nearly stoichiometric composition represented by tetragonal FeS or mackinawite.

Diffraction patterns for (102) of natural pyrrhotite are in general not simple but obscure excepting those observed especially in the region without iron deficiency. Taking into account of x-ray, thermal and microscopic data of the natural pyrrhotite from the Tsumo mine, Japan, Sugaki *et al.* (1962) classified the patterns of (102) into (1) the single type and (2) and (3) the splitted of which the last is convertible to the first through heating at 500°C. According to their view, the pyrrhotites of the former type are likely to reveal such exsolution textures as are associated generally with chalcopyrite accompanying skeletal sphalerite, sphalerite including emulsoidal chalcopyrite, magnetite and native bismuth, while those of the latter type are lacking in these exsolution textures, the former being represented as the high-temperature type compared with the latter. As was already stated, the Type A revealing the single and moderately sharp patterns corresponds to those with little excess of sulfur in composition. It seems dangerous to consider only that by heat treatment at a high temperature above 500°C the composition with sulfur in excess, yielding rather complicated patterns, is changeable to that with sulfur in less amount, displaying the single patterns simply owing to divergence of sulfur. On the other hand, correspondence of the type of (102) reflections to the associated minerals has been confirmed neither through the present experiment nor through investigation on polished sections.

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