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Reduction of the Saturation Magnetization by Quenching and by Pressure Squeezing in Some Ferrimagnetic Compounds

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In order to clarify the origin of the magnetism of the ferrimagnetic compounds $CrS_{1.17}$, $FeS_{1.13}$ and γ-Fe_2O_3, the effects of quenching from high temperature and of pressure squeezing at various high pressures upon their magnetic properties were observed. The X-ray diffraction patterns of these compounds were also observed before and after quenching or pressure squeezing. It is concluded that the origins of magnetism in $CrS_{1.17}$ and $FeS_{1.13}$ are due to the ordered arrangements of vacant sites of cations. The effect of pressure squeezing in γ-Fe_2O_3 may be accounted for the intermediate ionic arrangement in the phase transition from γ-Fe_2O_3 to α-Fe_2O_3.

1. Introduction

From many studies it has been suggested that the origin of the spontaneous magnetization in some ferrimagnetic compounds may be due to the ordered arrangement of the vacancies of cations. It can, therefore, be expected that their ferrimagnetism will disappear when the ordered arrangement of vacancies is forced to be disordered one by some methods. More effective one among them may be the quenching from high temperature. By the pressure squeezing at room temperature, the disordered arrangement may also easily be obtained, though the disordered arrangement in this case may be rather complicated due to the complex behaviour of plastic deformation.

2. Experimental Results and Discussions

(1) *The quenching effects*

The origin of the spontaneous magnetization in $CrS_{1.17}$[1] may be due to the ordered arrangement of the vacancies of chromium ions. Thus the authors attempted to quench the compound from 1000°C to force it to the disordered arrangement. The quenching was done by letting the vacuum sealed specimen drop into the cold bath. As expected, the spontaneous magnetization of $CrS_{1.17}$ decreased remarkably to the order of magnitude of the paramagnetism as shown in Fig. 1.

After quenching, the superlattice lines of the X-ray powder pattern corresponding to the ordered arrangement of vacant sites of chromium ions disappeared, but fundamental crystal structure remained unchanged. From these results, it can be concluded that the disappearance of ferrimagnetism is not due to the phase transition or the decomposition of the compound, but to the disordered arrangement of vacant sites. The relation between the intensities of the magnetization at -120°C and the quenching temperature is shown in Fig. 2.

The magnetization at -120°C remained unchanged when the specimen was quenched from the temperature lower than 340°C, but decreased remarkably when the quenching

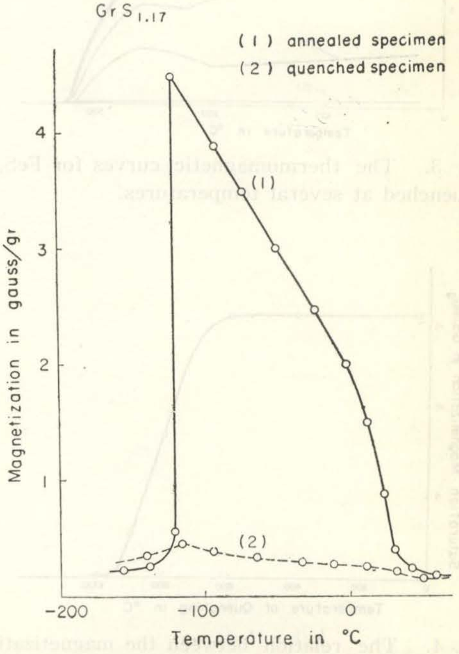

Fig. 1. Thermomagnetic curve for annealed and quenched sample, $CrS_{1.17}$.

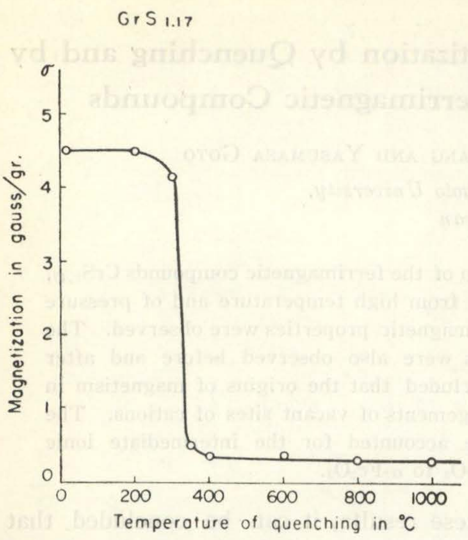

Fig. 2. The intensities of magnetization at -120°C for $CrS_{1.17}$ as a function of the quenching temperatures.

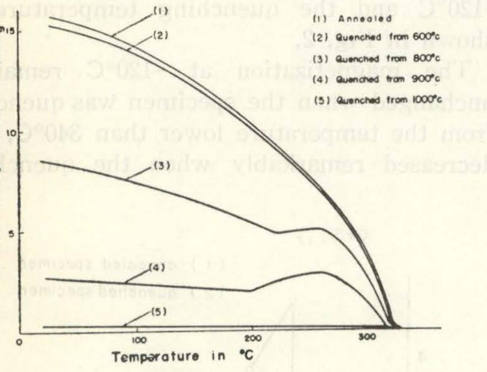

Fig. 3. The thermomagnetic curves for $FeS_{1.13}$ quenched at several temperatures.

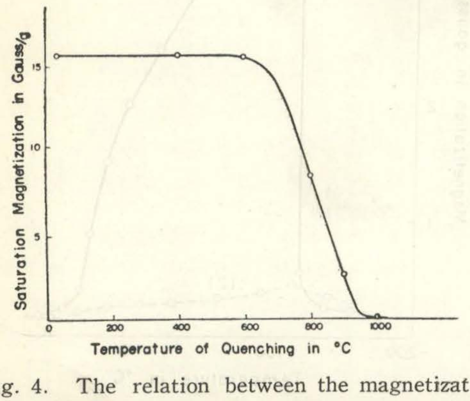

Fig. 4. The relation between the magnetization at room temperature for $FeS_{1.13}$ as a function of quenching temperature.

temperature was above 340°C. After quenching, no significant change in magnetization with time was observed at room temperature in any case.

As the orign of the spontaneous magnetization in $FeS_{1.13}$[2] is considered to be the same as in $CrS_{1.17}$, the authors attempted to quench it from various high temperatures in order to force the specimens to be in the state of disordered arrangement.

As expected, the spontaneous magnetization of $FeS_{1.13}$ decreased with increasing temperature of quenching and became the order of magnitude of the paramagnetism ultimately. As shown in Fig. 3, an anomalous peak in magnetic curve appears when the quenching temperature is high. These peaks may be considered to be the partial recoveries of the ordering of vacancies.

The relation of the magnetization at room temperature *versus* quenching temperature is shown in Fig. 4.

Although different results for order-disorder transition temperature have been obtained by some investigators[2], the authors found the transition temperature as about 750°C.

In the case of γ-Fe_2O_3 any change was not found in the thermomagnetic curve and in X-ray pattern by quenching from 300°C. As it begins to change to α-Fe_2O_3 above this

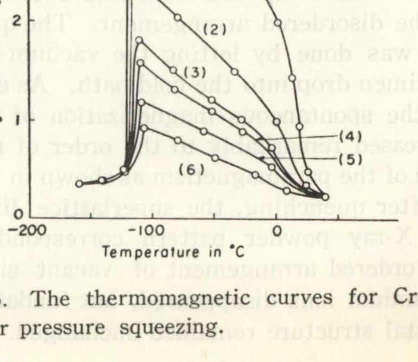

Fig. 5. The thermomagnetic curves for $CrS_{1.17}$ after pressure squeezing.

temperature, the quenching from higher temperature can not be carried out.

(2) *Pressure squeezing effects*

The specimens were squeezed between two tungsten carbide pistons in an apparatus of the Bridgeman anvil type. Each thermomagnetic curve was taken immediately after squeezing in the pressure range from 5,000 to 45,000 Kg/cm². The results for $CrS_{1.17}$ specimens are shown in Fig. 5.

The spontaneous magnetization decreased with increasing pressure and became the order of magnitude of the paramagnetism at the highest pressure. The superlattice lines of the X-ray pattern disappeared in this case as well, but the diffraction lines of the fundamental structure remained unchanged and became somewhat broader. These results correspond well with those of the quenching experiments. Thermomagnetic curves for $FeS_{1.12}$ after pressure squeezing are shown in Fig. 6.

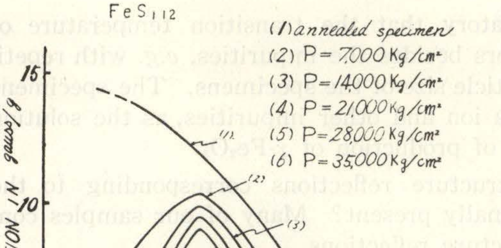

Fig. 6. The thermomagnetic curves for $FeS_{1.12}$ after pressure squeezing.

Roughly speaking, the spontaneous magnetization decreases considerably as in $CrS_{1.17}$ but its thermomagnetic curves show rather complicated behaviours. An anomalous peak appeared after the pressure was applied. These behaviours might be related to the ambiguous nature of magnetic properties of $FeS_{1.12}$.

From the results of the quenching and squeezing experiments, it is clarified that the origins of spontaneous magnetization of $CrS_{1.17}$ and $FeS_{1.13}$ are due to the ordered arrangement of vacant sites of cations. The reduction of magnetization by pressure squeezing could be accounted for by the shearing which includes the slip component along *c*-axis of fundamental hexagonal lattice, if these phenomena are caused only by the slip in crystal.

Also in the case of γ-Fe_2O_3 the spontaneous magnetization decreased with increasing pressure and its magnitude became about 90% of the original one at about 30,000 Kg/cm² as shown in Fig. 7.

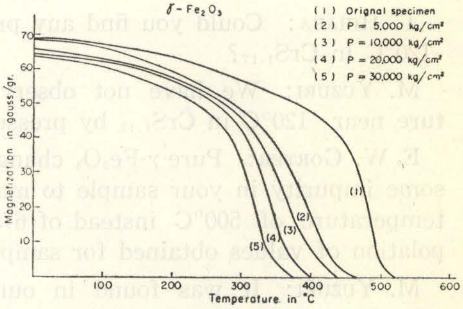

Fig. 7. Thermomagnetic curves of γ-Fe_2O_3 after pressure squeezing.

The transition temperature of γ-Fe_2O_3 shifted simultaneously to the lower temperature region by the amount of about 150°. In this case, the superlattice lines (110), (200) and (300)[3] also disappeared and the other diffraction lines became broader. These phenomena can never be explained simply by the exchange of iron atoms between tetrahedral and octahedral sites. When the pressure is applied uniaxially to the specimens, the plastic gliding in (111) plane would occur by the shearing effect of applied pressure as suggested by Kachi and Momiyama[4]. Then the stacking faults will be introduced in the slipped regions, in which the original f.c.c. framework of oxide ions changes to the h.c.p. stacking. The ionic arrangement thus attained can be considered as one of the intermedia in the phase transition to α-Fe_2O_3. In these regions, all iron ions must occupy the positions of the octahedral sites. So, the spontaneous magnetization would not occur in the slipped parts. Therefore, it is plausible that the reduction of magnetization takes place as a whole and the transition temperature shifts to lower temperature.

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DISCUSSION

T. Hihara: Could you find any pressure shift of the transition temperature near -120°C in $CrS_{1.17}$?

M. Yuzuri: We have not observed any shift of the magnetic transition temperature near -120°C in $CrS_{1.17}$ by pressure squeezing.

E. W. Gorter: Pure γ-Fe_2O_3 changes to α-Fe_2O_3 at about 300°C. I suppose you have some impurity in your sample to make it stable up to 500°C, and to give it a Curie temperature of 500°C instead of 675°C, which was obtained by A. Michel by extrapolation of values obtained for samples containing varying amounts of Na.

M. Yuzuri: It was found in our laboratory that the transition temperature of γ-Fe_2O_3 to α-Fe_2O_3 varies with several factors besides the impurities, *e.g.* with repetition of reduction and oxidation or with particle size of the specimens. The specimens used in this investigation scarcely contain Na ion and other impurities, as the solution containing Na was not used in the process of production of γ-Fe_2O_3.

E. W. Gorter: Are you sure all superstructure reflections corresponding to the tetragonal structure with $c/a=3$ were originally present? Many of our samples containing Na impurity do not show superstructure reflections.

M. Yuzuri: The superstructure lines (110), (200), (300) (according to the original cubic structure) were surely present before pressure squeezing.

S. Iida: In the case of pressure-squeezed γ-Fe_2O_3, the rate of diffusion of the cations will be large because of the presence of a large amount of disordered cation vacancies. Therefore, I am afraid that some kinds of phase changes may take place.