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## Neutron-diffraction study of $\gamma$ -Fe at high pressure

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Face-centered-cubic iron ( $\gamma$ -Fe) coherently precipitated in a single crystal of Cu has been studied by neutron diffraction at high pressures up to 0.9 GPa and in the temperature range from about 5 to 110 K. It undergoes antiferromagnetic ordering at  $67 \pm 2$  K at ambient pressure. The ordering temperature  $T_N$  monotonically decreases with increasing pressure following a relation  $T_N(\text{K}) = 67 - 12.8p - 11.1p^2 - 6.17p^3$ , where  $p$  is in units of GPa. The change of  $T_N$  in  $\gamma$ -Fe is discussed in terms of the volume change caused by pressurization or by alloying.

### I. INTRODUCTION

Iron exists in various forms. At ambient pressure, the bcc phase ( $\alpha$ -Fe) is stable up to 1183 K, and the fcc phase ( $\gamma$ -Fe) appears between 1183 and 1663 K. At higher temperatures but below the melting point (1807 K),  $\delta$ -Fe appears which crystallizes again in the bcc structure. Also, the hcp phase ( $\epsilon$ -Fe) exists at high pressures greater than 10 GPa. Although studies of the physical properties of each form in principle can be undertaken under thermodynamically stable conditions, those for  $\gamma$ -Fe have been made primarily on metastably retained specimens. The retention of  $\gamma$ -Fe to room temperature can be achieved by precipitation in a Cu matrix,<sup>1,2</sup> by film deposition on a Cu substrate,<sup>3</sup> or by alloying.<sup>4</sup> The precipitated and deposited  $\gamma$ -Fe is crystallographically coherent with the Cu crystal.

At cryogenic temperatures the precipitated  $\gamma$ -Fe undergoes antiferromagnetic ordering.<sup>5-12</sup> The magnetic structure was first shown by a neutron-diffraction study<sup>5</sup> to be composed of magnetic spins whose vectors are inclined at about  $19^\circ$  from the cube axes. However, a much more complicated structure, accompanied by a periodic lattice distortion, has been deduced from a recent neutron-diffraction study.<sup>12</sup> The antiferromagnetic ordering temperature  $T_N$  depends strongly on the size of the precipitates; with an upper bound of 67 K,  $T_N$  decreases with decreasing precipitate size.<sup>13</sup> In addition, the magnetic ordering is associated with a first-order structural phase transition<sup>14-16</sup> for precipitates above a critical size (15 nm).<sup>15</sup> Below the critical size, this structural transition becomes suppressed and, instead, only an incommensurate spin-density-wave (SDW) state appears.<sup>17</sup>

It can readily be expected that  $T_N$  will be altered also by an application of pressure. An expectation for a decrease in  $T_N$  of  $\gamma$ -Fe with increasing pressure can be de-

rived simply from the Bethe-Slater interaction curve<sup>18</sup> and this was verified by a high-pressure Mössbauer-effect study<sup>19</sup> yielding  $-5$  K/GPa. This Mössbauer-effect work studied precipitates with a size of 6 nm, which is significantly smaller than the critical size required for the presence of the structural phase transition. It is therefore likely that the Mössbauer-effect study dealt with the SDW state. The pressure dependence of  $T_N$  could be much different when the structural phase transition accompanies the antiferromagnetic ordering than that observed for the SDW state.

We report here a high-pressure neutron-diffraction study of  $\gamma$ -Fe precipitated in a Cu single crystal. The crystallographic coherence of the precipitates with the Cu crystal made it possible to undertake single-crystal neutron-diffraction studies. In our sample, the sizes of the precipitates were between 50 and 60 nm and  $T_N$  at ambient pressure was measured to be about 67 K, suggesting that the antiferromagnetic ordering was accompanied by the structural phase transition. However, owing to experimental difficulties associated with the "background" neutron scattering caused by the high-pressure cell, we did not carry out additional measurements of the structure to confirm this expectation. Hence, the present study is concerned only with the pressure effect on  $T_N$  and, we expect, at the same time, with the temperature for the structural phase transition of  $\gamma$ -Fe.

### II. EXPERIMENT

A Cu-Fe alloy containing 2.77 at. % Fe was prepared by melting the components in an induction furnace, followed by annealing at 1273 K for 5 h, quenching in water, and then annealing at 923 K for 44 h. With this heat treatment, the Fe was present as particles of 50 to 60 nm,<sup>15</sup> having the same orientation as the matrix Cu crystal. The crystal was machined into rods about 9 mm high

and 6 mm in diameter and the crystallographic [001] axis was parallel to the rod axis.

Each rod sample was encapsulated inside a micro cell made of an aluminum alloy. A single crystal of either NaCl or KCl was placed beneath the sample to serve as a pressure marker. Fluorinert, FC-75, was used as the pressure-transmitting fluid. The micro cell was placed inside a barrel-shaped cylinder made of  $ZrO_2$  and was loaded in a clamp-type high-pressure cell.<sup>20</sup> After clamping the load applied at room temperature, the high-pressure cell was attached to a displax refrigerator.

Neutron-diffraction measurements were carried out on the HB3 spectrometer at the High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory (ORNL). Also, the 5G as well as T1-1 spectrometers at JRR-3 of the Japan Atomic Energy Research Institute (JAERI) were used. The wavelengths of incident neutron beams were 0.2443 nm at HB3 and 0.2435 nm at 5G and T1-1, respectively. A graphite filter was used to reduce the  $\lambda/2$  intensity. The [001] axis of the crystal was oriented perpendicular to the neutron-scattering plane. After the sample was cooled below the temperature of the appearance of the magnetic satellite of  $\gamma$ -Fe, the intensity of the magnetic reflection was measured while warming the sample.

After finishing a series of such measurements at a fixed pressure, the sample was unloaded and retrieved to the ambient pressure. The sample was then encapsulated again and loaded for a subsequent pressurization, or otherwise, a new sample was pressurized.

### III. RESULTS AND DISCUSSION

Figure 1 shows intensity contours of the magnetic reflection measured on the (001) scattering plane near 1 1 0 at 0.2 GPa and 10.0 K. The magnetic reflection is peaked at 1.01 1.01 0 in a reciprocal lattice unit of the Cu matrix, with a crosslike shape typical of the magnetic scattering of the low-temperature phase of  $\gamma$ -Fe.<sup>12</sup> Such

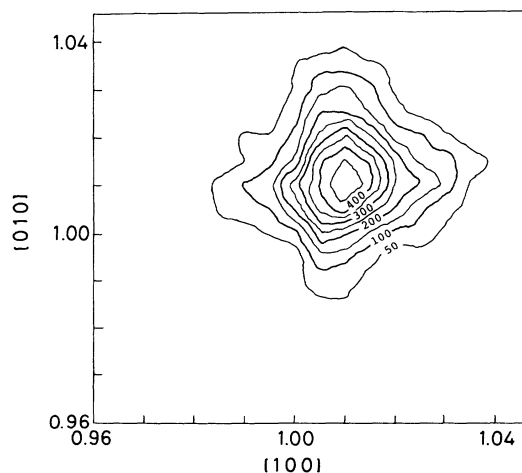


FIG. 1. Contour plots of neutron intensities of  $\gamma$ -Fe around the 1 1 0 reciprocal lattice point measured at 0.2 GPa and 10.0 K. The plots were obtained by subtracting 80.0 K data from 10.0 K data. The numbers on the contours are shown in a unit of neutron counts per min.

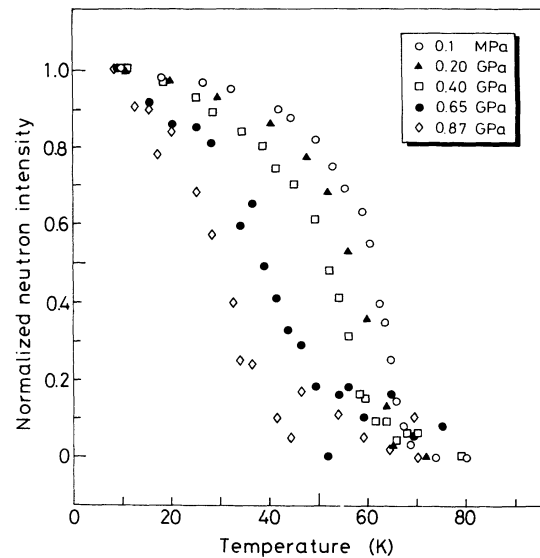


FIG. 2. Neutron intensities of the magnetic peak of  $\gamma$ -Fe plotted against temperatures at various pressures.

measurements performed at temperatures from 10 to 80 K provide the temperature dependence of the magnetic peak intensity and give an estimate of  $T_N$ .<sup>21</sup>

The peak intensities of the magnetic reflection measured at various pressures are plotted in Fig. 2 against temperatures. At ambient pressure,  $T_N$  is located at  $67 \pm 2$  K, in agreement with previous studies.<sup>6,9,13,15</sup> At pressures 0.20 and 0.40 GPa, the feature of the plots is very similar to that at ambient pressure. It, however, becomes somewhat different at 0.65 and 0.87 GPa. Yet the transition points can be defined, obviously showing that they decrease with increasing pressure.

We note that the sample pressurized to 0.87 GPa exhibited, after removing the pressure, an intensity-vs-temperature behavior very similar to that of the sample before compression.<sup>21</sup> Also, there occurred no change in the line profile of the Bragg peak before and after the compression. These results suggested that the precipitates size remained unchanged by the pressurization.

Figure 3 shows plots of  $T_N$  against pressure. The smoothed curve in Fig. 3 follows a relation

$$T_N(\text{K}) = 67 - 12.8p - 11.1p^2 - 6.17p^3,$$

where  $p$  is in GPa. Figure 3 also shows a result from Mössbauer-effect study which gives a slope of  $-5$  K/GPa in a pressure range to 4 GPa.<sup>19</sup> There are apparent differences between the two experiments in both ambient pressure  $T_N$ 's and their pressure derivatives. The Mössbauer-effect study places  $T_N$  at 46 K at ambient pressure, significantly lower than that from our study as well as those of other works.<sup>6,9,13,15</sup> The low value of  $T_N$  can be ascribed to the small size (6 nm) of the precipitates studied, as suggested from the strong dependence of  $T_N$  on precipitate size.<sup>13</sup> This precipitate size is also much smaller than the critical size<sup>15</sup> for the presence of the structural phase transition. Therefore, the SDW state instead of the structural phase transition is presumably as-

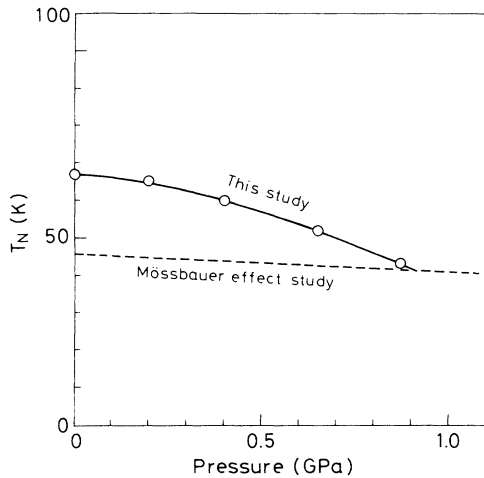


FIG. 3. Change of the Néel temperature of  $\gamma$ -Fe as a function of pressure. Also shown for comparison are data from a Mössbauer-effect study (Ref. 19).

sociated with the antiferromagnetic ordering in this case.

The difference in the changes of  $T_N$  with pressure becomes notable when the fractional changes in  $T_N$  are plotted against fractional volume changes. Figure 4 shows such plots derived from high-pressure (Ref. 19 and this study) and alloy studies.<sup>16</sup> The volume change is caused either by pressurization or by alloying. A general trend is that  $T_N$  increases with increasing volume. In the pressure domain, the fractional change in  $T_N$  is negative

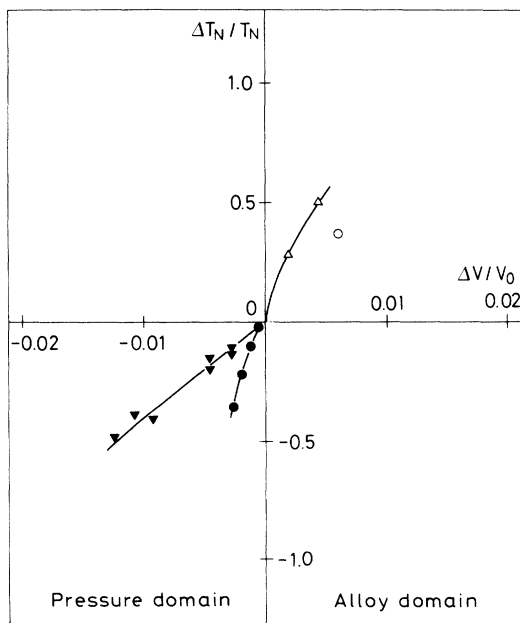


FIG. 4. Normalized antiferromagnetic ordering temperature as a function of fractional volume change. ●  $\gamma$ -Fe(Cu) (present study); ▼  $\gamma$ -Fe(Cu) (Ref. 19); △  $\gamma$ -FeCr(Cu) (Ref. 16); ○  $\gamma$ -Fe(Cu<sub>97</sub>Au<sub>3</sub>) (Ref. 16). The amounts of the volume change in the pressure domain were derived from pressures described and the bulk modulus of  $\gamma$ -Fe given in Ref. 23. The volume expansion in the alloy domain was derived from pertinent description for each alloy in the reference.

and the slope of the present study (associated with the structural phase transition) is more than double that of the Mössbauer-effect study.<sup>19</sup>

The fractional change in  $T_N$  is positive in the alloy domain, where we show data from alloys of  $\gamma$ -Fe with Cr in the Cu matrix and also from  $\gamma$ -Fe in the Cu<sub>97</sub>Au<sub>3</sub> matrix.<sup>16</sup> The volume expands with alloying in these alloys, either in the precipitates or in the matrix. The initial slope for the  $\gamma$ -FeCr alloy appears to be close to that for our high-pressure study. Although the datum of  $\gamma$ -Fe in Cu<sub>97</sub>Au<sub>3</sub> alloy falls at a point less inclined than the line for  $\gamma$ -FeCr alloy, it is still far from a positive extrapolation of the Mössbauer-effect study. Thus, the volume dependence of  $T_N$ 's in these alloys is closer to our high-pressure neutron-diffraction study than to the Mössbauer-effect study. Furthermore, the structural phase transition also accompanies the antiferromagnetic ordering in these alloys.<sup>16</sup> If our presumption is correct that the Mössbauer-effect study<sup>19</sup> dealt with the SDW state, then the volume dependence of  $T_N$  differs markedly according to whether the antiferromagnetic ordering is associated with the structural phase transition or the SDW state.

The different dependence of  $T_N$  on volume (hence, pressure) would in turn lead to an expectation that the two lines in Fig. 3 would meet at approximately 1.0 GPa. It is of interest to know if our  $\gamma$ -Fe sample encounters the SDW state around this pressure regime. The relevant experiments were undertaken at 0.7 GPa. Figure 5 shows diffraction patterns in the vicinity of the 1 0 0 reciprocal lattice point taken under pressure and at ambient pressure. If the SDW state existed, a pair of satellites should appear at  $q \sim \pm 0.1$ .<sup>17</sup> In the high-pressure pattern, Fig. 5(a), such satellites are perceivable, whereas no such reflection can be observed in the ambient pressure pattern, Fig. 5(b). The peak at  $q=0$  in Fig. 5(a) presumably is due to resolution smearing of the satellites above and

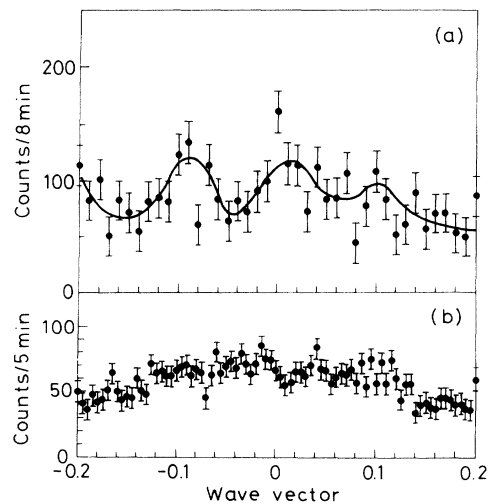


FIG. 5. Neutron-diffraction patterns of  $\gamma$ -Fe around the 1 0 0 reciprocal lattice point obtained by scanning along the [010] direction: (a) at 0.7 GPa from difference between 4.8 K and 110 K data; (b) at ambient pressure and 14.0 K outside the high-pressure cell.

below the scattering plane. Also, the satellite intensities exhibited a clear temperature dependence. An attempt to study the sample at 1.0 GPa failed due to a break of the ZrO<sub>2</sub> cylinder. Although the data in Fig. 5(a) are insufficient to claim the existence of the SDW state, pressurization may induce a change in the antiferromagnetic ordering of  $\gamma$ -Fe from structural transition associated into SDW associated.

The neutron intensity of the antiferromagnetic phase before being normalized (Fig. 2) actually exhibits a rapid drop upon the application of pressure.<sup>21,22</sup> The decrease in intensity can be ascribed to a pressure-induced decrease in the magnetic moment in the antiferromagnetic phase of  $\gamma$ -Fe. Such a decrease in the magnetic moment with pressure is in qualitative agreement with first-principles calculations.<sup>23-26</sup> Our observation, although limited to the scattering near the 1 1 0 reciprocal lattice point, did show an appreciable weakening of the magnetic reflection as the pressure was raised toward 0.9 GPa. It is likely that the nonmagnetic state could appear in a manner suggested by the calculations. However, no quantitative statement can be made of the disappearance of the magnetic peak intensity within this study because the peak was slightly contaminated by the powder peak of the high-pressure cylinder.<sup>20</sup>

#### IV. CONCLUSION

Measurement of neutron intensity of the (110) magnetic peak of  $\gamma$ -Fe precipitates at high pressure and low temperature has elucidated the pressure dependence of the antiferromagnetic ordering temperature which in our case is associated with a structural phase transition. The pressure dependence of the ordering temperature has been found to be different from an earlier Mössbauer-effect study,<sup>19</sup> which presumably dealt with the SDW-associated ordering. The difference is rationalized from plots of the ordering temperatures of various  $\gamma$ -Fe families against fractional volume changes caused by either compression or alloying.

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