Phase transitions in samarium at high pressures

W. Y. Dong, T. H. Lin, K. J. Dunn,* and C. N. J. Wagner
Department of Materials Science and Engineering, School of Engineering and Applied Science, University of California, Los Angeles, California 90024
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The electrical behavior of Sm was studied for pressures up to 43 GPa and temperatures from 430 down to 2 K. The two Néel temperatures at ambient pressure are found to move toward each other as the pressure increases and finally merge into one at the dhcp phase. At room temperature, we found that Sm transforms to a new phase, presumably fcc, at about 12 GPa. The phase line between the dhcp and the new phase appears to tie with the cusp of the bcc phase line.

I. INTRODUCTION

One of the most interesting behaviors of rare-earth metals is the structural similarity among elements in the series. The rare-earth series is characterized by a gradual filling of the $4f$ shell. For most of these elements, the $4f$ shell is located deeply within the atom and is highly localized. Hence the outer regions of different rare-earth-metal atoms are very similar to each other, and one would expect similar behavior in their solid modifications. As one proceeds from the heavier elements towards the lighter ones, one can realize a structure sequence of (hcp$\rightarrow$Sm type$\rightarrow$$dhcp\rightarrow$$f$cc). The same sequence is also exhibited by all individual elements when subjected to high pressure and by alloys between different trivalent rare-earth metals.

Johansson and Rosengren[1] proposed a general phase diagram for the rare-earth-metal series based on the existing experimental information on the phase boundaries of the solid-solid and solid-liquid modifications for all trivalent rare-earth metals. This phase diagram illustrates a common trend in crystal structures for the rare-earth elements and provides a guide for exploring the predicted phase transitions which have not yet been found experimentally.

We chose samarium as the candidate of our investigation because its electrical behavior contains many features associated with phase transitions. At ambient condition, samarium has a nine-layer, i.e., *ABABCBCAC*..., close-packed structure (Sm type). Alstad *et al.*[2] found that the resistivity of samarium shows two slope changes at 14 and 106 K associated with antiferromagnetic transitions. Early work by Jayaraman and Sherwood[3] indicates that samarium undergoes a phase transformation to the dhcp phase at pressures around 4 GPa and temperatures near 350 °C. The new phase has a Néel temperature of 27 K. Stager and Drickamer[4] studied the electrical resistance behavior of Sm at 296 and 77 K up to about 20 GPa. At room temperature, they found an inflection in the resistance slope at about 5 GPa and a distinct drop in resistance at around 13 GPa (16–17 GPa in the old pressure scale). Later, Nakaue[5] studied the pressure-temperature diagram of Sm and other rare-earth metals up to 9 GPa and 700 °C. In this paper, we report our measurements on the electrical behavior of Sm for pressures up to 43 GPa and temperatures from 430 down to 2 K. The two Néel temperatures at ambient pressure are found to move toward each other as the pressure increases and finally merge into one at the dhcp phase. At room temperature, we found that Sm transforms to a new phase, presumably fcc, at about 12 GPa. The phase line between the dhcp and the new phase appears to tie with the cusp of the bcc phase line observed by Jayaraman.[6]

II. EXPERIMENTAL RESULTS

The pressure equipment used in this investigation was a cryogenic clamp-type sintered-diamond-compact anvil apparatus. The experimental procedure and pressure calibration have been described elsewhere.[7–9] Basically, the pressure calibration is established by several pressure calibrants with electrical resistance abnormalities associated with known phase transitions. The pressure uncertainty is about ± 2 GPa.

The samarium metal of 99.9% purity was obtained from Alfa Products. The samples were prepared under white oil by rolling freshly cut metal chips with a carbide scriber to form thin foils about 0.07 mm thick. Specimens of a rectangular shape of approximately 0.13×0.6 mm^2 were cut and placed in the high-pressure cell. The sample was encased in the cell made by two disks and a ring of pyrophyllite. Gold electrodes were extended from both ends of the sample to the conducting part of the opposed anvils. Current was then passed through the sample to monitor its resistance behavior as a function of temperature and pressure.

Figure 1 shows a typical result of the electrical resistance behavior of Sm as a function of pressure at room temperature for both loading and unloading cycles. Our room-temperature result is different from that of Stager and Drickamer,[4] but it is quite similar to their result at liquid-nitrogen temperature. At about 4.5 GPa, our room temperature run shows a kink in the resistance versus pressure curve, consistent with their observation. This kink is perhaps related to the phase transition for Sm from Sm type to dhcp.[5] However, we did not observe the distinct resistance drop at about 13 GPa reported by

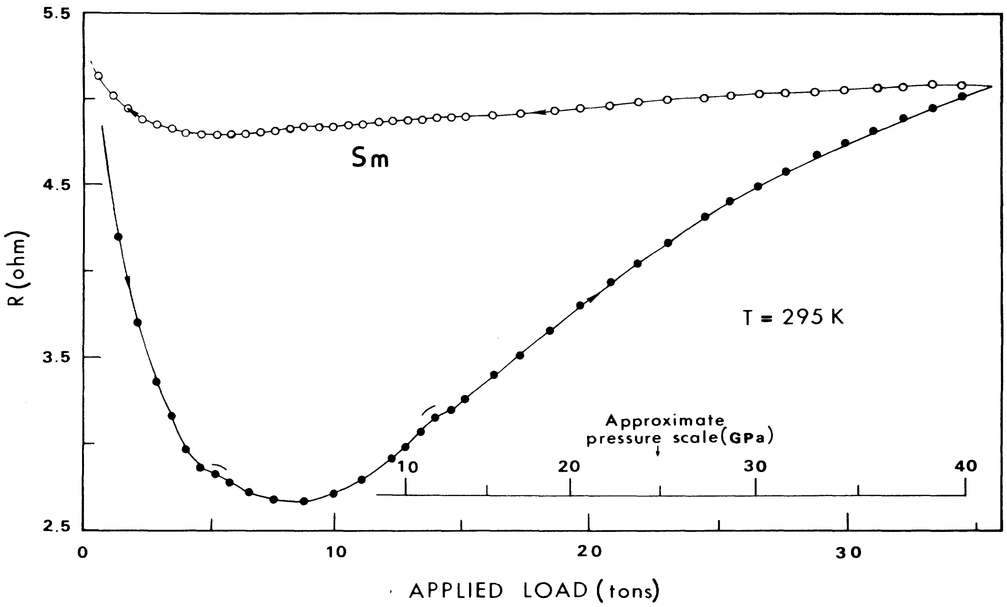

FIG. 1. The electrical resistance versus pressure at room temperature for Sm.

them. Instead, we found that the electrical resistance reaches a minimum at around 6 GPa, increases again, and exhibits another kink in the increasing resistance at about 12 GPa, which was observed repeatedly in every run we made. We believe this second kink is associated with the phase transition from dhcp to a new phase, presumably fcc. We shall discuss this in detail later.

To study the electrical resistance behavior of Sm as a function of temperature at various pressures, we first load the sample in the clamp press to the desired loading at room temperature, then insert the clamped rig into a cryogenic dewar, lower the temperature to liquid-helium temperature and below, and monitor the electrical resistance of the sample during the slow warm-up process. The clamp press, designed to be temperature compensated, gives nearly constant cell pressure during the slow warm-

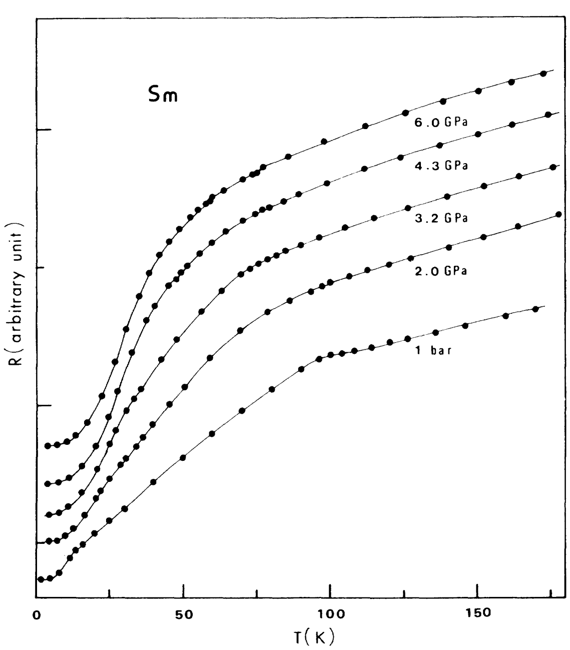

FIG. 2. The electrical resistance versus temperature for Sm at ambient pressure and four pressures 2, 3.2, 4.3, and 6 GPa.

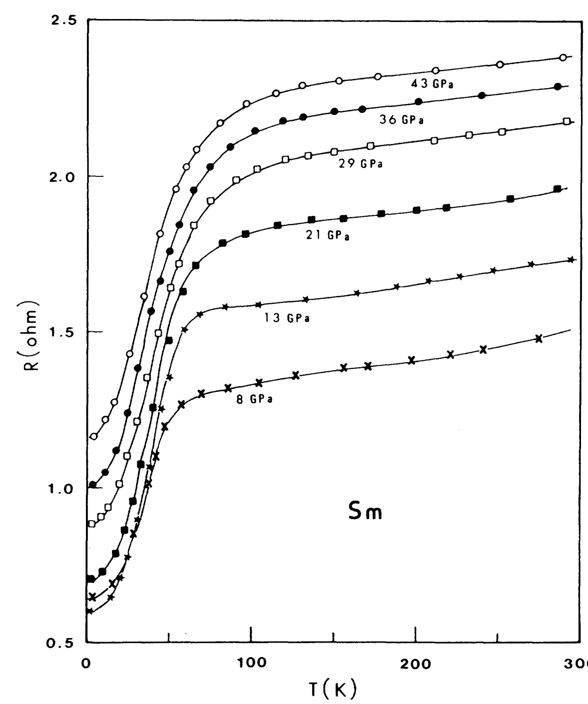

FIG. 3. The electrical resistance versus temperature for Sm at different presures; 8, 13, 21, 29, 36, and 43 GPa.

up process. The sample resistance was averaged with the exciting current in both forward and reverse directions to remove any thermal emf.

Figure 2 shows the R versus T behavior for Sm at ambient pressure along with four isobaric runs, i.e., 2, 3.2, 4.3, and 6 GPa. The run at ambient pressure was a 4-lead measurement. One can easily see the slope changes at 14 and 106 K which are related to the antiferromagnetic transitions.[2] The four isobaric runs were made by using the tungsten carbide anvils. They were the result of a continuous run accomplished by successfully loading the clamp press between each temperature cycle to liquid-helium temperature. As the pressure increases, the slope changes associated with the two antiferromagnetic transitions become less pronounced but still discernible. At higher pressure, these two temperatures move closer toward each other.

Figure 3 shows six isobaric runs, i.e., 8, 13, 21, 29, 36, and 43 GPa, made by using the sintered-diamond-compact anvils. Here, only one Néel temperature was observed. In Fig. 4, the derivatives of the electrical resistance of Sm with respect to temperature are plotted as functions of temperature at various pressures. The arrows shown in the figure indicate where the Néel temperatures are located. At pressures 2, 3.2, 4.3, and 6 GPa, two distinctive changes in dR/dT versus T observed. At higher pressures, only one was found.

Based on our present results and the early work by Nakaue[5] and Jayaraman,[3,6] we put together a phase diagram for Sm as shown in Fig. 5. The two resistance slope changes associated with the antiferromagnetic transitions are shown in the P-T diagram. At pressures above 7 GPa at low temperatures, only one resistance slope change was found, consistent with the Sm-dhcp phase line determined by Nakaue.[5] The cusp on bcc phase line[6] was thought to be the joining point of the phase line between dhcp and Sm type. With the x-ray work by Nakaue,[5] we know that the dhcp and Sm-type phase line is at a much lower location. Thus, the cusp on the bcc phase line must be a joining point for the phase line between dhcp and a new phase at higher pressures. This brings us back to our earlier observation for Sm at room temperature in which the electrical resistance of Sm shows a slope change at about 12 GPa, indicating that Sm has transformed from dhcp to a

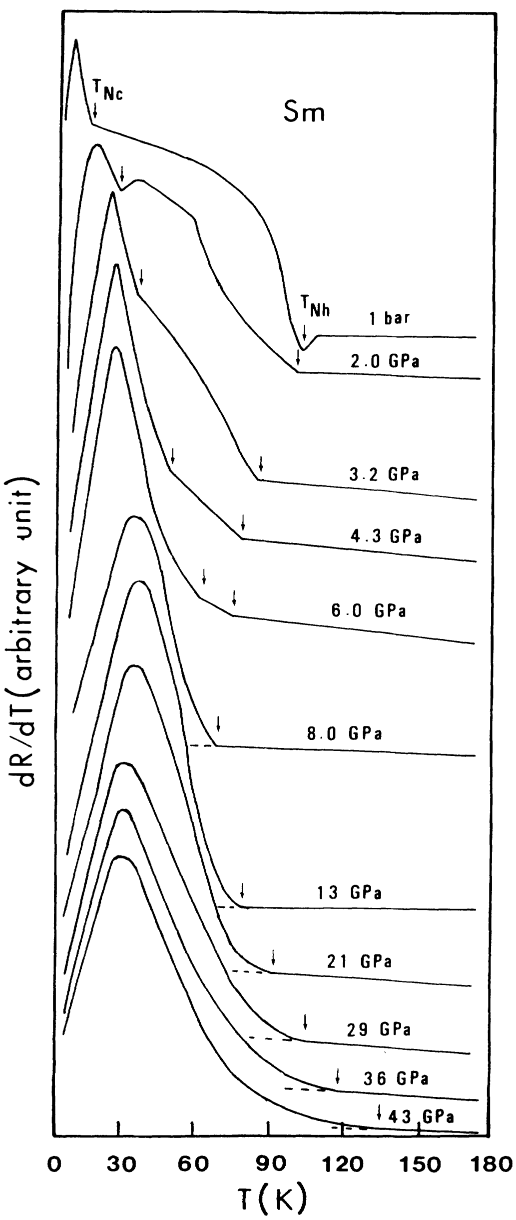

FIG. 4. The temperature dependence of dR/dT of Sm at different pressures.

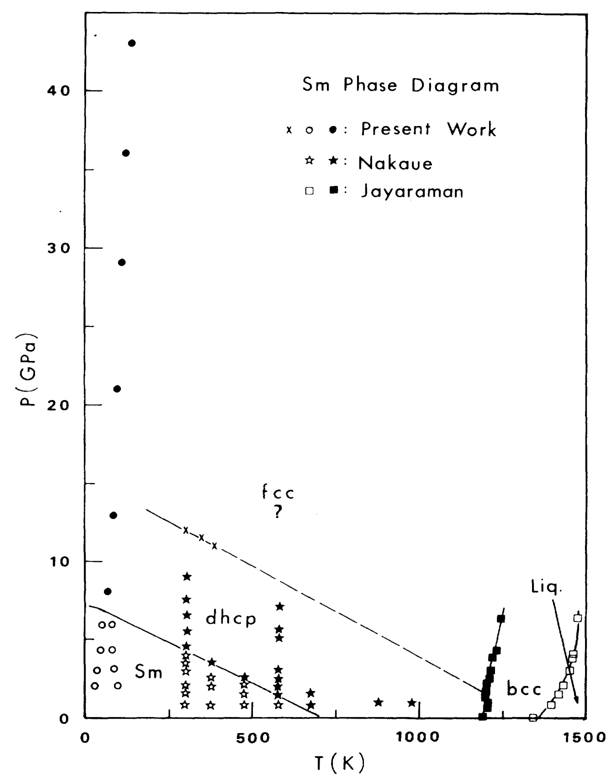

FIG. 5. The suggested phase diagram for Sm.

new phase. If the phase line between this new phase and the dhcp phase extrapolates to the cusp on the bcc phase line, we should be able to observe a similar slope change in electrical resistance of Sm at pressures lower than 12 GPa and temperatures higher than room temperature.

To test this hypothesis, we did three experiments: two isobaric runs at pressures less than 12 GPa, i.e., 11 and 11.5 GPa, and one isobaric run at 14 GPa. The results are shown in Fig. 6. The Sm sample was first compressed to the desired pressure and was held at that pressure while the temperature was increased. Indeed, we found the slope change occurred at 378 K at 11 GPa, and at 348 K at 11.5 GPa. These two points on the P-T diagram along with the point at room temperature and 12 GPa are on a straight line which extrapolates to the cusp on the bcc phase line. In the experiment of 14 GPa, we first compressed the Sm sample at room temperature to pass the slope change in the electrical resistance at 12 GPa and held the pressure constant at 14 GPa while increasing the temperature. To our surprise, we still found a slope change in R versus T at a temperature near 335 K. Such a slope change in R versus T is, however, not reversible, and not repeatable in the second temperature cycle. This behavior suggests that the transformation of Sm from the dhcp to the new phase, which took place at 12 GPa and room temperature, was probably incomplete up to 14 GPa. Further increase in temperature helped the completion of the phase transformation.

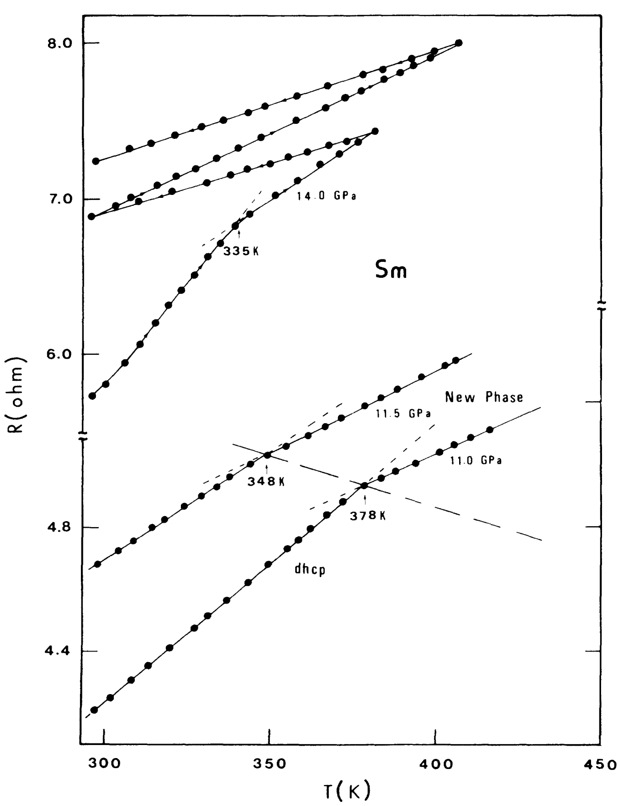

FIG. 6. The temperature dependence of R of Sm at different pressures for temperatures between 300 and 430 K.

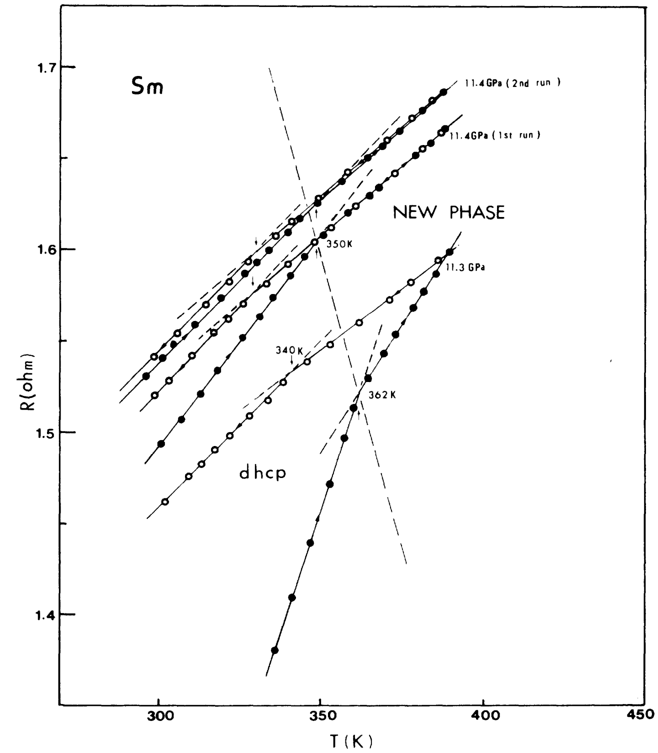

FIG. 7. The temperature dependence of R of Sm at pressures 11.3 and 11.4 GPa.

To investigate the hysteresis of the transition, we repeated the runs at 11.3 and 11.4 GPa with both warming and cooling cycles. The slope change of the electrical resistance for the run at 11.3 GPa took place at ~ 362 K while warming up. The reverse transition occurred at ~ 340 K while cooling down isobarically. For the isobaric run at 11.4 GPa, two temperature cycles were carried out. Both results are shown in Fig. 7. The forward transition temperatures were indicated by arrows pointing upward, and the reverse transition temperatures by arrows pointing downwards. The phenomena again demonstrate that the phase transition is thermally activated. Some activation energy is required to initiate the transition.

III. DISCUSSION

In the early work by Jayaraman and Sherwood,[3] Sm was found to transform from Sm-type to dhcp phase after being subjected to 4 GPa and 350 °C for 15 min. and returned to room temperature and ambient pressure condition. Apparently, the dhcp phase is metastable at ambient condition. Their magnetic measurements indicate that the Néel temperature for this metastable phase has shifted to 27 K. This is to be compared with our electrical measurements which indicate a Néel temperature around 48 K at 4.3 GPa as shown in Fig. 4. Our result shows that the higher the pressure the higher the Néel temperature it has. The fact that the relaxed, metastable dhcp phase has a lower Néel temperature of 27 K at ambient pressure is compatible with this general behavior.

The different polymorphic phases of Sm, i.e., Sm type, dhcp, and fcc, are all of close-packed structure, but each of them has a different atomic stacking sequence. In transforming from one phase to the next high-pressure phase, some atomic layers must shift positions. It appears that temperature aids pressure in effecting the transformation. This was observed by Jayaraman and Sherwood[3] and was also demonstrated in Fig. 6 of the present work.

In the proposed phase diagram for Sm shown in Fig. 5, the dhcp-fcc phase line extrapolates to about 15 GPa at low temperatures. If this indeed is the case, then the antiferromagnetic transition appears to continue to be existent in the fcc phase to pressures as high as 43 GPa.

Our finding of the possible fcc-dhcp phase line for Sm and together with the x-ray results by Nakaue,[5] have modified the general phase diagram proposed by Johansson and Rosengren[1] somewhat.

The position of the phase diagram of Nd relative to that of Sm was determined by fitting the bcc phase lines of Nd to the corresponding lines of Sm, with the restriction that no Sm-type structure overlapped the Nd phase diagram. The relative positions of the phase diagram of Nd and Pr were tied in with that of La by fitting the known transitions for Nd and Pr from dhcp to fcc structure to the known phase line of the corresponding transition in La. Now that we know Sm has the proposed Sm-dhcp and dhcp-fcc phase lines as shown in Fig. 5, if this is true, it would mean that the phase diagrams of Nd, Pr, and La have to be shifted toward the phase diagram of Sm by approximately 2 GPA. From the x-ray work of Nakaue,[5] we know that the Sm-dhcp phase line for Sm is at a much lower, P,T location in the phase diagram than originally thought when the Sm-dhcp line was assumed to tie in with the cusp of the bcc phase line. Hence, the shift of approximately 2 GPa for Nd phase diagram will not result in an overlap with the Sm-type structure.

Johansson and Rosengren's general phase diagram for the rare-earth metals exhibits a rich variety of behavior and contains many inferences of phase transitions of rare-earth elements yet unobserved experimentally. Our present work on Sm is a step toward a better understanding of the general behavior of the rare-earth-metals series.

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*Permanent address: Chevron Oil Field Research Company, La Habra, CA 90631.

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