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Pressure effect on superconductivity of vanadium at megabar pressures

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The superconducting transition temperature T_c of vanadium has been measured up to 120 GPa by using a superconducting quantum interference device vibrating coil magnetometer. It was found that T_c increased with pressure with a coefficient of $dT_c/dP=0.1$ K/GPa and at the maximum pressure onset of superconductivity reached 17.2 K, the highest T_c among the elemental metals reported so far. Large signal to noise ratio was obtained for detecting the superconductivity of vanadium at megabar pressures in a diamond-anvil cell.

The recent development of new techniques for electric and magnetic measurements in a diamond-anvil cell (DAC)[1–4] enables us to increase the pressure range of investigation to very high values where the electronic states of substances change substantially from those at ambient pressure as a result of significant decrease in volume or structural changes. The subject in this pressure range focuses mainly on superconductivity especially for simple molecular solids expected to show pressure-induced superconductivity at megabar pressures.[5–7] For some transition metals, on the other hand, superconducting transition temperatures T_c's were measured at very high pressures to compare the experimental results with theoretical prediction.[2]

In this paper, we report the pressure dependence of the T_c of vanadium up to 120 GPa. Superconductivity of the vanadium group (V, Nb, Ta) has been well studied because it shows a relatively high T_c, and for Nb $T_c=9.25$ K is the highest value among the elemental metals. Unlike Nb and Ta, V ($T_c=5.3$ K at ambient pressure) has a large positive pressure coefficient of T_c and T_c increases with pressure in the pressure range investigated so far. Smith[8] measured the T_c of V as a function of hydrostatic pressure up to 2.4 GPa and found a linear increase in T_c with $dT_c/dP=0.062 \pm 0.003$ K/GPa, comparable with the theoretical values including spin-fluctuation effects. Subsequently, Brandt and Zarubina[9] observed a monotonic increase in T_c up to 18 GPa using an ice-bomb and mechanical press. Recently, Akahama *et al.*[10] made electrical resistance measurements using a Drickamer cell up to 49 GPa to investigate to what extent the monotonic increase in T_c with pressure would hold. They found that T_c increased linearly with a coefficient of $dT_c/dP=0.096$ K/GPa at pressures above 18 GPa and T_c reached 9.6 K at their maximum pressure, which was comparable to that of Nb at ambient pressure. They interpreted such a behavior of T_c under pressure as a result of the suppression of the fluctuations of the electron spins through the broadening of the *d*-band width. The spin fluctuation is connected with the occurrence of paramagnon, which counteracts superconductivity.[11] This fact stimulated us to carry out experiments at much higher pressures so as to establish experimentally whether such a linear increase in T_c would still hold or if the sign of dT_c/dP would change at higher pressure.

We used a small DAC of a pressure-clamp type, all parts of which were made of hardened Cu-Be alloy. Alignment and tilt adjustment mechanism for diamond anvils was not provided so as to obtain enough space for the detection coil around the anvils. Both anvils were set so that they were facing as parallel as possible by rotating and displacing the anvil on the fixed piston before the anvil was glued to it. We stamped out vanadium disks of 30 or 40 μm in diameter as a sample from a foil of 25.4 μm in thickness with a purity of 99.95%, which were put in a hole of Re gasket together with ruby powder for pressure determination. No pressure medium was used.

dc magnetic susceptibility χ_{dc} was measured by using a superconducting quantum interference device (SQUID) vibrating coil magnetometer (VCM) (Ref. 12) to determine the T_c of V. Even though we deal with samples of very small sizes in a DAC, rather large signals of perfect diamagnetism due to superconductivity can be obtained when a disk-shaped sample is used and measurements are made along the axis of the disk. The signal associated with the superconducting transition is proportional to $Hv/2r(1-D)$, where H, v, r, and D are applied magnetic field, volume of the sample, effective radius of the SQUID detection coil, and demagnetization factor of the sample, respectively,[13] showing that a large enhancement of the signal occurs when the sample gets thinner and D approaches 1. The use of a SQUID VCM as a sensing device enables us to make high-sensitive magnetic measurements with good signal-to-background noise ratio for extremely small samples in a DAC. This is because the location of the detection coil of a SQUID magnetometer can be adjusted to have maximum sensitivity above the gasket

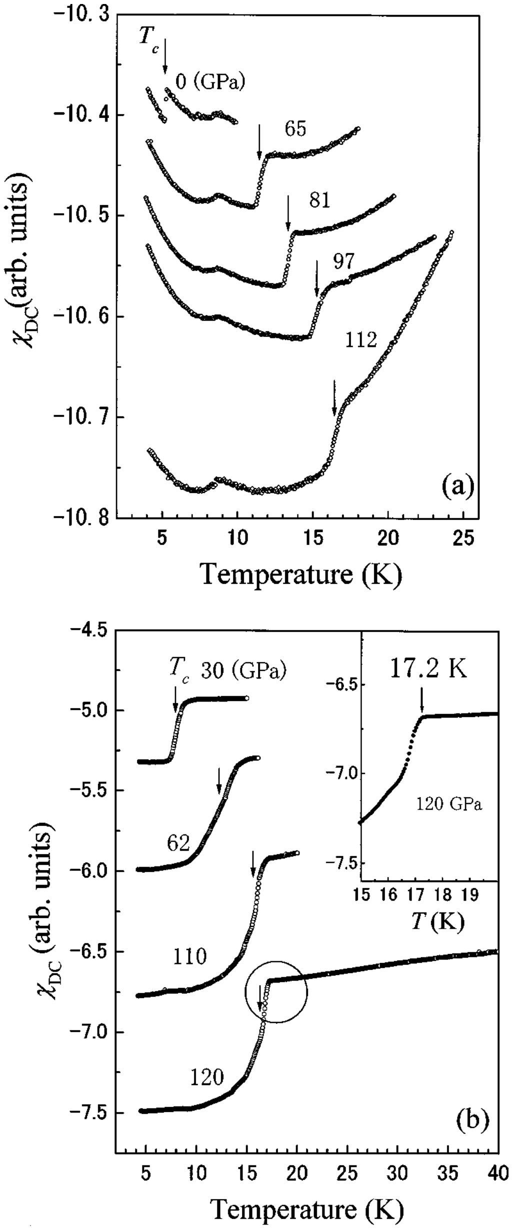

FIG. 1. Temperature dependence of dc susceptibility of vanadium at various pressures. Measurements were made for different samplings; run A (a) and run B (b). Arrows show T_c's determined as the midpoint of the transition. The scale of the ordinate is the same for both the figures. The inset of (b) shows the expanded view around the onset of superconductivity at 120 GPa.

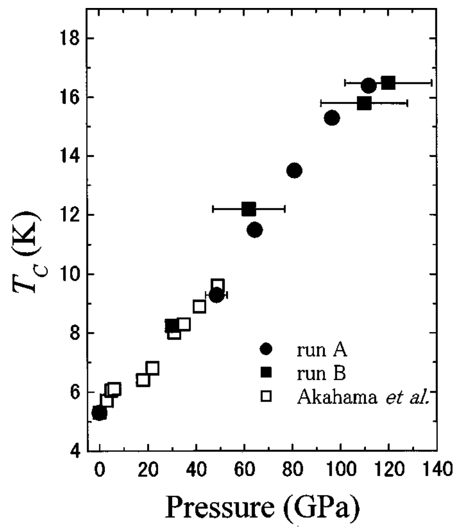

FIG. 2. Pressure dependence of the T_c of vanadium.

where the gradient of the magnetic flux due to the sample magnetization takes a maximum value. Besides, the background signal decreases with distance from the detection coil at a higher rate than that in the case of magnetic-flux detection.

Measurements of χ_{dc} were made at temperatures above 4 K, below which the signals changed abruptly due to the superconductivity of Re used for a gasket.

Figure 1(a) shows the temperature dependence of the χ_{dc} of V at various pressures up to 112 GPa measured with increasing temperature at a magnetic field of 3 Oe after zero-field cooling, which we call run A. A small peak at around 8.5 K, which appears on all the data and the magnitude and the temperature are almost independent of pressure, may come from the Re gasket. Although there was a small increase in signals at high and low temperatures due to the background signal, clear transitions were observed in all curves. The signals at high pressures are large compared with those at ambient pressure and their magnitudes are almost independent of pressure. This is because the shape of the sample changes to a very thin disk as a result of a large plastic deformation perpendicular to the load in the initial compression. Figure 1(b) shows the result for another run, B. Although the magnitudes of the signals at ambient pressure are nearly the same for both runs, the signals at high pressures for run B increase more than about 12 times as large as those for run A, indicating a much larger enhancement of the signal occurring in run B. This may result from the difference in the amount of the ruby powder covering the sample, which changes the thickness of the sample when compressed together with the ruby powder. The value of the demagnetization factor may also be affected largely by nonuniform distribution of the ruby powder, which causes the variation of the local thickness of the sample. Detection of such large signals suggests that much reduction of the sample size, which would be needed at much higher pressure, may be possible for the measurement of T_c of the superconductor. As for the sharpness of the transition, the transition width for run B was about 4–5 times as large as that for run A. This indicates a larger pressure distribution in the sample for run B, which was consistent with the results of the ruby fluorescent measurement at room temperature. The inset of Fig. 1 (b) shows the expanded view around the onset of superconductivity at 120 GPa. As shown in the figure, the temperature of the onset reaches 17.2 K, the highest T_c among the elemental metals reported so far and comparable to that of compressed sulfur[5] in the second metallic phase at 157 GPa.

Figure 2 shows the pressure dependence of T_c up to 120 GPa, determined as the temperature at the midpoint of the transition. Previous results are also included in this figure. Surprisingly, T_c is still increasing with pressure over a very wide range of pressure and T_c reaches 16.5 K at 120 GPa, which is more than three times as large as that at ambient pressure. In contrast to the case of Nb where large anomalies in $T_c(P)$ are observed at 5–6 GPa and 60 GPa, there are no abrupt changes in $T_c(P)$ for V. A large and monotonous increase in T_c suggests the pressure effect on the spin fluctuation holding over a large compression of the lattice constant, $\Delta a/a = 0.122$ at 120 GPa,[14] or another mechanism enhancing the electron-phonon coupling working under high pressure. Recent calculations of electron-phonon coupling for the vanadium group,[15] however, show a good agreement of the calculated values with those obtained by specific-heat measurements without considering paramagnon contribution. A small steplike increase could be observed in $T_c(P)$ at about 60 GPa but the change is so small that a detailed measurement will be required to confirm the existence of the ‘‘step.’’ Since there is no structural change for V up to 160 GPa (Ref. 14) and an anomaly of T_c corresponds to a change in the electronic structure at the Fermi energy, such a discontinuity in $T_c(P)$ may provide a clue to understanding the interplay of the parameters necessary for calculating the microscopic T_c. Expansion of the pressure range to higher values as well as detailed measurements will be needed to obtain more information about the behavior of $T_c(P)$. Further theoretical investigations of *ab initio* calculations of the superconducting transition temperature will also be needed for explaining such a high T_c.

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