Superconductivity in a New High-Pressure Phase of Scandium

J. Wittig and C. Probst[(a)]
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, Germany

and

F. A. Schmidt and K. A. Gschneidner, Jr.
Ames Laboratory-DOE and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

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A phase transformation is observed in scandium metal at a pressure of approximately 170 kbar as seen from a rise of the electrical resistance by a factor of 4. The high-pressure phase (Sc II) is a superconductor. T_c is found to increase with pressure from $\simeq 50$ mK at 186 kbar to $\simeq 0.35$ K at 210 kbar. Experimentally, sintered diamond anvils have been used in a six-lead Bridgman setup with internal manometer.

Scandium is the lightest element among the s^2d^1 transition metals Sc, Y, La, and Lu. The inset in Fig. 1 refers to the corresponding portion of the periodic table. Hexagonal close-packed Sc has previously not been found to be superconducting, either at ambient pressure or at high pressure up to approximately 150 kbar.[1] Conversely, the heavier trivalent elements, i.e., Y, La, and Lu, unanimously show a strong increase of T_c with pressure. Figure 1 contains the experimental T_c-P curves for La, Y, and Lu and, in addition, the data for the new high-pressure modification, Sc II, which will be presented and discussed in more detail below. As seen from Fig. 1, the interesting question arose whether Sc would fall in line with the other trivalent transition metals by eventually showing superconductivity at some very high pressure. It has been suggested that antiferromagnetic spin fluctuations (as opposed to ferromagnetic spin fluctuations in Pd) may be responsible for the lack of superconductivity in Sc.[2,3] In this Letter we report on first results of an investigation of Sc up to 210 kbar and down to a lowest temperature of 50 mK. Following the work of Bundy[4] an appreciable extension of the pressure range has been accomplished by employing anvils made from sintered diamond ("Compax"[5]) rather than tungsten carbide. A phase transformation has been observed at approximately 170 kbar by monitoring the electrical resistance. The high-pressure phase, Sc II, turned out to be superconducting.

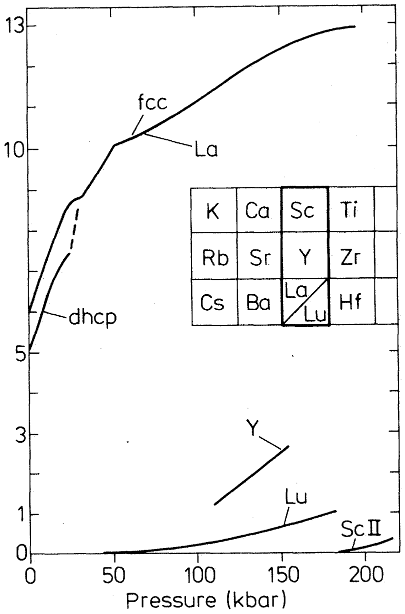

FIG. 1. Superconducting T_c vs pressure for La, Lu, and Y (after Ref. 1). The line labeled Sc II is a smooth fit of the data in Fig. 3. The inset features the elements in the third column of the periodic table.

Bridgman anvils have been fabricated from commercial wire-drawing-die blanks[5] by grinding with the appropriate diamond wheels. The anvil flat-face diameter was chosen to be 2 mm. The pressure cell was a scaled-down version of a cell previously described in detail.[6] Six platinum electrodes are employed to measure current and voltage drop of the Sc sample and, simultaneously, of a Pb sample serving as a superconducting manometer in the low-temperature run. The pressure is adjusted at room temperature. The mechanical press and the ^{3}He/^{4}He dilution-refrigerator cryostat have been described elsewhere.[7]

A sample of pure Sc had been further refined by the electrotransport process.[8] The resulting bar of Sc was of extraordinary purity. The resistance ratio R_{300K}/R_{4K} exceeded 600. Mass spectroscopic analysis revealed a very low concentration of magnetic or at least possibly magnetic impurities. The following traces (in weight ppm) were detected: $Cr \simeq 3$, $Mn < 0.1$, $Fe \simeq 10$, $Co < 1$, $Ni \simeq 1$, and $Gd \simeq 10$. Other rare-earth metals are below 1 ppm. As judged from other systems, the Gd contamination will lead to a reduction of T_c of $\simeq 10$ mK. No such estimate is possible for the influence of Fe on T_c, but at higher Fe concentrations ($\geqslant 25$ ppm) Kondo scattering has been reported.[9]

Figure 2 shows the room-temperature resistance of Sc (full circles) as a function of press load. Also shown is the pressure dependence of the resistance of the Pb sample (open symbols). The marked rise of the resistance indicates the Pb I → II phase transition at 130 kbar. The resistance of Sc I increases slightly with pressure. At approximately 170 kbar the resistance rises by a factor of the order of 4. The reverse transformation has also been observed in different experiments. It shows strong hysteresis partly caused by the hysteretic pressure-load relationship in this apparatus.

For the same pressure cell the inset of Fig. 3 shows four superconducting transitions (circles) shifting to higher temperatures with increasing pressure. As judged from the behavior of the room-temperature resistance in Fig. 2, the sample had completely transformed into Sc II at 186 kbar. In Fig. 3 the same transitions are displayed as a function of the superconducting transition temperature of the Pb manometer. In either case, the bars and midpoints indicate those temperatures where the normalized resistance R/R_n equals 0.9, 0.1, and 0.5, respectively. The pressure dependence of T_c has heretofore not been calibrated up to such high pressures. A provisional pressure scale has therefore been established as follows. GaP undergoes a semiconductor-to-metal transition at 220 kbar.[10,4] We have pressurized a cell containing samples of GaP and Pb until GaP became metallic. Upon cooling nearly isobarically to low temperatures, a superconducting $T_c = 1.73$ K was observed for Pb at 220 kbar[11] (as compared to 7.2 K at 1 bar). Previous experiments revealed that T_c of Pb is 3.6 K at 130 kbar.[12] By simply linearly interpolating between these pressure fixed points we arrive at the approximate pressure scale displayed at the top of Fig. 3. For a comparison, the data of Fig. 3 are also shown in Fig. 1 and labeled Sc II.

There is evidence that the hcp phase (Sc I) is also a superconductor with $T_c \lesssim 0.1$ K at pressures slightly below the transformation to Sc II.

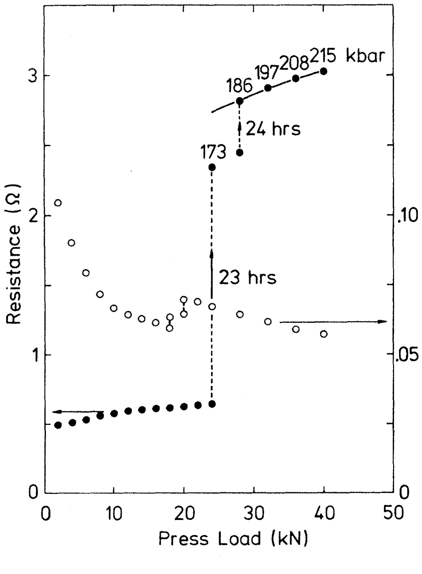

FIG. 2. Room-temperature resistance vs press load for Sc (filled circles) and Pb (open circles). Dashed lines indicate drift with time. The phase transition Sc I→II occurs at approximately 170 kbar upon increase of pressure.

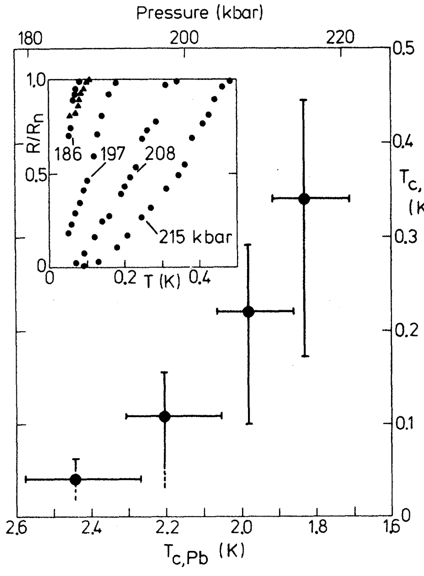

FIG. 3. Superconducting transitions of the high-pressure phase Sc II vs T_c of the Pb manometer (lower scale) for the pressure cell of Fig. 2. The upper scale is a preliminary pressure scale as discussed in the text. The inset shows the normalized superconducting transitions as a function of temperature.

As seen from the horizontal bars in Fig. 3, the pressure inhomogeneity $\Delta P/P$ is typically of the order of 10%. This fact enables one to study samples where both phases are present simultaneously. According to Fig. 2, the room-temperature resistance had settled at a value conspicuously below the resistance of pure Sc II at a nominal pressure of 173 kbar indicating an estimated remainder of approximately 20% Sc I. Preceding the four experiments with pure Sc II as described above, this mixed-phase sample has been studied for superconductivity at the pressure of 173 kbar. A matching 20% superconducting transition was detected at $\simeq 0.1$ K (inset of Fig. 3, triangles). We ascribe this partial superconducting transition to the anticipated 20% Sc I in the sample. As can be seen from Fig. 3, the T_c of Sc II is expected to be below the measuring limit of 50 mK at this pressure. The result is backed by a similar observation in an independent experiment. We conclude that Sc I is also a pressure-induced superconductor, as are Lu and Y, with a maximum T_c of the order of 0.1 K at $\simeq 170$ kbar. Above that pressure Sc II becomes stable. T_c of Sc I is slightly higher than for Sc II at a given pressure in the transition region. This can be directly seen from the inset of Fig. 3, where the triangles (Sc I) are at slightly higher temperatures than the nearby partial transition of pure Sc II at a 13-kbar higher pressure.

From a systematic point of view we consider it to be extremely satisfying that Sc shows pressure-induced superconductivity in line with Lu and Y (Fig. 1). Certainly, the quantitative T_c-P dependence for Sc I has to be worked out in the future. The experiments must be extended to appreciably lower temperatures than 50 mK and should aim at more homogeneous pressures. In somewhat anticipating these results, it is apparent that the properties of Sc, Y, and Lu at high pressure represent a new interesting piece of the systematics of the d-transition metals. Our observation of superconductivity in Sc at $\simeq 200$ kbar gives no direct clue as to the presence of spin fluctuations[2,3] at ambient pressure. However, it now appears rather unlikely that there exists a special mechanism in Sc (and not in Y and Lu) responsible for the lack of superconductivity at normal pressure.

Several interesting questions arise. Will the elements Y and Lu also exhibit phase transformations near 200 kbar characterized by a comparatively large increase of the room-temperature resistance? So far, there are faint indications for a possible phase change in Y as discussed elsewhere.[1] Interestingly enough, the two adjacent elements Ti and Zr (Fig. 1, inset) both possess corresponding high-pressure phases.[13] For Lu, which is probably actually the proper element[1] below Y in the periodic table, a crystallographic phase transition has been reported at 230 kbar.[14] It is thus quite possible that the latter transformation is the direct counterpart of the new Sc I-II transformation. Resistivity measurements up to such high pressures are therefore of interest for Lu and Y in order to investigate whether the analogous transformation occurs. Supposing that Y and Lu do show strictly corresponding phase transformations as Sc, what will be the behavior of $T_c(P)$ near the transition? Is there, as for Sc, only a relatively small discontinuity at the transition point with T_c steeply rising again in phase II? Is the anticipated common crystal structure of the high-pressure phases in fact the samarium-type structure as previously suggested[14] for Lu II? For comparison, what is the crystal structure of La at pressures of the order of 200 kbar?

Investigations of the band structure have revealed a considerable increase of the pd electron-phonon matrix element with pressure for several early transition metals.[15,16] These theoretical results are thus qualitatively in agreement with the observed rise of T_c for the trivalent transition metals. For a further comparison of theory and experiment it would be interesting to have theoretical predictions for the pressure dependence of the electron-phonon coupling constant for all the metals in the inset of Fig. 1. A search for superconductivity at high pressure in the alkali metal Rb is now being carried out.

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[a]Present address: ZTF, Bayer. Akademie d. Wissenschaften, D-8046 Garching, Germany.

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Chemisorption of Atomic Hydrogen on Large-Nickel-Cluster Surfaces

Thomas H. Upton and William A. Goddard, III
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology,
Pasadena, California 91125

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First-principles Hartree-Fock calculations are reported for binding of a hydrogen atom at high-symmetry sites of low-index faces of Ni surfaces (using an Ni_{20} cluster as a model). Chemisorption energies increase with ligancy of the binding site, with bond energies of 1.6, 2.8, 3.2, and 3.0 eV for onefold, twofold, threefold, and fourfold sites, respectively. A reverse trend is found for ω_e with values of 275, 170, 150, and 73 meV for ligancies of 1, 2, 3, and 4, respectively.

Despite numerous experimental[1-3] and theoretical investigations,[4,5] there is currently great uncertainty concerning the qualitative and quantitative aspects of H-atom chemisorption on transition metals. Here we report first-principles Hartree-Fock calculations for the interaction of atomic hydrogen with a twenty-atom Ni cluster. This cluster possesses chemisorption sites corresponding to most of the important sites on the (100), (110), (111), and (112) surfaces of this metal.

From calculations on small clusters of Ni atoms (up to eight) we have found the following: (i) The lowest states have a localized $3d^9$ configuration on each Ni atom with bonding that is dominated by delocalized 4*s*-like orbitals.[6-8] (ii) The use of delocalized Hartree-Fock orbitals (as in usual band calculations) leads to large errors in describing the *d* orbitals with an overemphasis of 3*d*-4*s* mixing.[9] Allowing these orbitals to be localized, we find lower total energies and reduced mixing of 4*s* and 3*d* orbitals, permitting a factorization of the electronic states into a set of conduction-band (delocalized 4*s*) orbitals and the localized 3*d* orbitals consisting of five orbitals and nine electrons for each Ni atoms. In addition, we have found that the role of the 3*d* orbitals in determining the shape of the conduction-