

cylinder type cell of 3.0 mm diameter. This slight increase in cell dimensions facilitates the mounting of an additional lead sample which is used as a manometer by recording its superconducting transition temperature¹⁷. Calibration in the pressure range up to 10 kbar is done by comparison with the data of Jennings and Swenson on Sn and In¹⁸, which were considered to be the most reliable. Above 10 kbar direct pressure reference points are hard to attain. Solid-solid phase transitions which prove to be useful at room temperature must be used with care because of the temperature dependence of the transformation pressure and of pressure changes during cooling. In the pressure regime up to 40 kbar we therefore rely primarily on the linearity of our strain gauge — bent beam combination. We have checked this instrument with the phase transformation in thallium whose temperature dependence, measured between 300 and 90 °K, was found to be linear and was extrapolated to 0 °K. The value of 34.5 kbar so obtained is in good agreement with the extrapolated strain gauge data (35.0 kbar). In this regime we estimate the accuracy of the pressure measurement to be $\pm 1.5\%$. For pressures between 40 and 80 kbar we use the calibration data obtained in this laboratory¹⁹. In this region the uncertainty rises with pressure up to an estimated value of $\pm 4\%$.

The gain in maximum pressure (80 kbar as compared with 50 kbar in the earlier equipment) is mainly due to a hard steel ring of 6.0 mm o.d. which is pressed into the softer main cylinder. This ring usually suffers fine cracks when a pressure of 50–60 kbar is reached, but still distributes the force and reduces it at its circumference.

Alloys

Nine binary alloys from Nb₄₀Zr₆₀ to Nb₇₃Mo₂₇ were made from starting materials specified as follows: Nb 99.9% rod, Koch-Light Labs.; Mo 99.95% rod, Johnson-Matthey; Zr 99.5% sponge, W. C. Heraeus. All metals were outgassed before alloying by melting in an electron beam furnace in vacuum of 10^{-5} – $5 \cdot 10^{-5}$ Torr. The same vacuum conditions were maintained during preparation of the alloys which was performed by casting four times. Maximum weight loss was 4.5% which probably did not affect the composition. The buttons were cut on a diamond saw and cold rolled to ribbons of 0.05 mm thickness from which the rectangular samples (2.5 × 0.1 × 0.05 mm) were prepared. The transition temperatures of the Zr-rich niobium alloys were higher than

18 Jennings, L. D., Swenson, C. A.: Phys. Rev. **112**, 31 (1958).

19 Eichler, A., Wittig, J.: Z. angew. Phys. **25**, 319 (1968).

those reported by Hulm and Blaugher²⁰ by 0.1 to 0.5 °K. For this reason the transition to superconductivity was studied for some of these alloys by an induction method in addition to the usual resistive method. Rods were used as well as ribbons; the latter were mounted in different ways (straight along the axis of the induction coil and rolled around this axis). The maximum scatter of the measured T_c amounted to only ± 0.08 °K. Further support for the homogeneity of the alloys is derived from the sharpness of the transition observed in specific heat measurements²¹.

Special efforts were made to purify niobium. This was achieved by electric heating of 0.03×4 mm² ribbons in ultra-high vacuum (better than 10^{-10} Torr) for five hours, gradually approaching the melting point. For this purpose that part of the glass vacuum apparatus which contained the ribbon was immersed in liquid nitrogen, thus acting as an additional cryopump. The residual resistance ratio $\Gamma = R_{10^\circ\text{K}}/R_{300^\circ\text{K}}$ was lowered in this way from 1/20 to 1/2100.

Measurements of Γ (ribbons) and Vickers hardness HV (buttons) for all alloys are plotted in Fig. 1 versus number n of valence electrons per atom at zero pressure*. Except for the sharp singularity for pure niobium, both quantities show no peculiarities, which is indicative of having a single phase in each of the two binary alloy series, Nb-Zr and Nb-Mo. This is corroborated by X-ray diffraction data which show, in accordance with¹⁰, pure β -phase (*bcc*) for the complete alloy series. Values of the lattice constant obey Vegard's law²² with change in slope at $n=5$ (Fig. 1).

Two ternary alloys $\text{Nb}_{96}\text{Zr}_2\text{Mo}_2$ and $\text{Nb}_{63}\text{Zr}_{14}\text{Mo}_{23}$ with $n=5.0$ and 5.09, respectively, were also made. As expected, both hardness and resistance ratio differ from those for pure niobium and a Nb-Mo alloy of same n . It is interesting, however, that the lattice constant for $\text{Nb}_{63}\text{Zr}_{14}\text{Mo}_{23}$ falls off a Vegard's line by an amount far outside experimental error. In all relevant diagrams the data points of the ternary alloys are printed as triangles.

For niobium it had been noticed that the variation of T_c with pressure is very sensitive to lattice defects generated when pressure is applied at temperatures of liquid helium¹⁷. This is now found to be true also for the niobium-rich alloys $\text{Nb}_{96}\text{Zr}_4$, $\text{Nb}_{96}\text{Mo}_4$, and for the ternary alloy $\text{Nb}_{96}\text{Zr}_2\text{Mo}_2$. Irreversibilities due to the above effect were avoided in these cases by application of pressure at temperatures near 300 °K,

* n is thus defined by the chemical composition. It is not to be confused with the actual electron concentration which may be pressure dependent.

20 Hulm, J. K., Blaugher, R. D.: Phys. Rev. **123**, 1569 (1961).

21 Dummer, G.: Unpublished.

22 Vegard, L.: Z. Physik **5**, 17 (1921).