Superconductivity in amorphous 3*d*-transition-metal alloy films

M. M. Collver
Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, Campinas, São Paulo, Brasil

R. H. Hammond
Stanford University, Hansen Physics Laboratory, Stanford, California 94305
(Received 22 February 1978)

Superconducting transition temperatures in amorphous 3*d*-transition-metal alloy films of V-Ti and V-Cr have been found to increase with the number of electrons per atom in agreement with the T_c behavior found in the 4*d* and 5*d* series.

Superconducting transition temperatures of amorphous or highly disordered transition-metal alloys were found to exhibit a nearly linear decrease on both sides of a T_c peak which lies in the middle of the 4*d* and 5*d* series for alloys composed of nearest and next-nearest neighbors in the Periodic Table.[1,2] Our purpose here is to present an extension of these systematic results to amorphous 3*d*-transition-metal alloys, notably V-Ti and V-Cr with up to 5-at.% chromium. The T_c behavior was found to be in accord with the other transition-metal series. A monotonic increase in T_c was observed over the limited range of data examined.

The alloy films were prepared by single-source electron-beam evaporation onto liquid-helium cooled sapphire substrates in a vacuum of 10^{-7} Torr. Film thicknesses were 1000–1200 Å, deposited at a rate of approximately 100 Å/sec. Four point probe measurements were made to obtain the transition temperatures. The films were then heated to 300 K while resistance was monitored, cooled back to 4.2 K, and T_c was remeasured. Electron diffraction of a film ($Ti_{0.41}V_{0.59}$) with no resistance change upon annealing to 300 K revealed three broad diffraction rings. From this and the inability to observe grains by electron microscopy down to an approximate resolution limit of 25 Å, we infer that the material is amorphous. Films with smaller concentrations of a second element exhibited a considerable and often abrupt decrease in resistance upon heating, and were found to have the normal bcc structure. From the change in resistance we have inferred that these films were amorphous in the as-deposited state. The composition of the alloy films was determined by electron microprobe analysis as described previously.[1]

The transition temperature for the as-deposited V-Ti and V-Cr films are shown in Fig. 1 with the crystalline alloy T_c data[3] indicated by the dashed line. T_c's less than the corresponding crystalline values are found for V-Ti alloys and $V_{0.99}Cr_{0.01}$, with a slightly larger value for $V_{0.95}Cr_{0.05}$. The observed behavior in T_c is consistent with that found for the 4*d*-transition-metal alloys (Zr-Nb, Zr-Mo, and Nb-Mo) in that the broad T_c maximum in the crystalline data of V-Ti is replaced by lower T_c values which increase monotonically with the $\bar{z}$ over the limited concentration range examined. The T_c of 1.52 K for Cr is that of Schmidt *et al.*[4] for ion-beam sputtered films codeposited with a xenon-ion beam on substrates near room temperature. These films had a bcc structure. We can expect that the T_c of amorphous Cr may be larger on the basis of a comparison with its isoelectronic neighbor Mo, which exhibits an enhanced T_c in the disordered bcc structure,[5] but even larger T_c's in the amorphous state[1] (as evidenced by an abrupt resistance change upon annealing). On the basis of the absence of any significant resistance change upon annealing, we

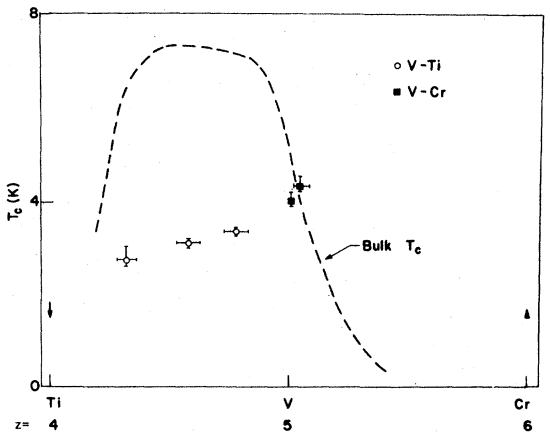

FIG. 1. Superconducting transition temperature vs number of electrons per atom ($\bar{z}$) for V-Ti and V-Cr films, as deposited.

infer that our Cr films were prepared in a bcc structure, as found by electron microscopy at 300 K. Thus it appears that the presence of impurities, or, as was found necessary in the case of Mo, a very high deposition rate, may be necessary to stabilize an amorphous or even more disordered structure. Under the conditions of preparation used here we estimate a maximum impurity concentration of 0.3 at. %. In general, evaporation from a single source of V-Cr resulted in a film of either pure Cr or one of high V concentration (95 and 99 at.%) once the Cr concentration in the alloy was nearly exhausted. We attribute this to the large vapor pressure of Cr compared to V. The inability to prepare films with more Cr by this technique prevented locating a possible T_c maximum between V and Cr, as well as the extrapolation of V-Cr data to a T_c for amorphous Cr. The vapor-pressure problem is even worse for V-Mn, and though V-Fe may be attempted, there is a sizeable vapor-pressure difference as well as possible charge transfer and/or magnetic effects.[2] Two-source evaporation is thus required to resolve the details regarding a peak in T_c for the 3*d* alloys.

The transition temperatures after annealing to 300 K are shown in Fig. 2. The arrow at the top of the figure indicates the alloy which exhibited an amorphous diffraction pattern and negligible resistance change. Despite this there is an increase in T_c for this film as well as for the other V-Ti films. We feel that the V-Cr data may be representative of the amorphous state because upon annealing the T_c's of both films change toward the crystalline values, i.e., the $V_{0.99}Cr_{0.01}$, film increases in T_c and the $V_{0.95}Cr_{0.05}$ film decreases, as shown in Fig. 2.

While we may not expect the same behavior in the 3*d* alloys as found in the 4*d* and 5*d* series, because of magnetic effects, we see that, initially at least, Cr does not depress T_c in the amorphous alloys. Furthermore the occurrence of superconductivity in Cr,[4] which we may prefer to regard as due to disorder, suggests that it may extend to

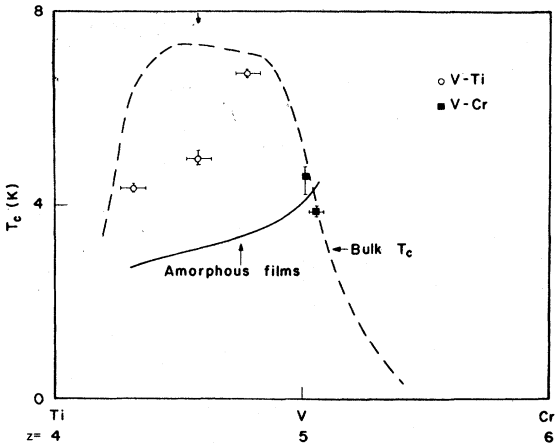

FIG. 2. Superconducting transition temperature vs $\bar{z}$ for annealed (to 300 K) V-Ti and V-Cr films.

Cr-Mn alloys. The monotonically increasing T_c behavior observed here for these materials is in accord with the T_c characteristics observed for the 4*d* and 5*d* transition metals. Although there is no definitive evidence for a T_c peak, one expects a maximum in the 3*d* series on the basis of the observed increases in T_c for low $\bar{z}$ and the presence of magnetic effects which suppress T_c on the high $\bar{z}$ side. The question of the presence of a T_c maximum as found in the amorphous 4*d* and 5*d* series, which is believed to be independent of magnetic effects, is clearly an open question for the 3*d* transition metals. Systematic experimental data on the variation of the amorphous T_c across the 3*d* series could provide stimulus for theoretical consideration of the electron-phonon parameter with strong Coulomb correlations included. Recent theoretical considerations have had some success in describing the electron-phonon parameters of the 4*d* series, where Coulomb correlations are weak.[6,7] With some assumptions, the theory is consistent with the measurements of the amorphous T_c across the 4*d* series.[1]

[1]M. M. Collver and R. H. Hammond, Phys. Rev. Lett. 30, 92 (1973).
[2]M. M. Collver and R. H. Hammond, Solid State Commun. 22, 55 (1977).
[3]W. L. McMillan, Phys. Rev. 167, 331 (1968).
[4]P. H. Schmidt, R. N. Castellano, H. Barz, B. T. Matthias, J. G. Huber, and W. A. Fertig, Phys. Lett. 41A, 367 (1972).
[5]J. J. Hanak and J. I. Gittleman, in *Proceedings of the International Conference on Science of Superconductivity* (North-Holland, Amsterdam, 1971), p. 555.
[6]W. H. Butler, Phys. Rev. B 15, 5267 (1977).
[7]D. G. Pettifor, J. Phys. F 7, 1009 (1977).