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Study of some hydrogenated vanadium-based *A*15 compounds

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The degrees of hydrogenation in V_3Ga, V_3Ge, and V_3Si were determined. The effects of hydrogen on the superconducting transition temperature T_c, the lattice parameter, and the pressure dependence of T_c were measured. The results will be discussed and compared with those of other hydrogenated and radiation damaged *A*15 compounds.

I. INTRODUCTION

The influence of defects on the properties of high-temperature *A*15 superconductors has been an active area of research in the past few years.[1] Independent of their origins, defects are found to cause a universal degradation[2,3] of the superconducting transition temperature T_c, an expansion[3] of the lattice parameter a_0 and the removal[4,5] of the normal-state anomalies which are often characteristics of a high-T_c superconductor. Because of the reversible effects of irradiation, studies on the irradiated compounds have provided valuable data correlating the universal T_c degradation with the reduction in long-range order[1,2] and the subsequent modifications[6,7] in the electron band structure due to defects. Unfortunately, the high level of radioactivity of the irradiated samples has made difficult the experiments from which microscopic information can be extracted. As a result, our current understanding[1] of the defect effect on high-temperature superconductivity remains macroscopic.

Recently, quite similar to defects introduced by irradiation, hydrogen was found to generate reversibly a large reduction of T_c and an expansion of a_0 in Nb_3Sn (Ref. 4) and Nb_3Ge (Ref. 8), and the arrest of the low-temperature structural transformation in the former.[4] In view of the nonradioactive nature of and the locatability of the H atom in a hydrogenated compound, a systematic study on the hydrogenated *A*15 compounds is particularly appealing. Therefore we have investigated the hydrogenation in V_3Ga, V_3Ge, and V_3Si. Due to the lower atomic number V, these V-based hydrogenated *A*15 compounds are more suitable than the Nb-based ones for our future near-edge x-ray absorption study[9] where the role of local symmetry recently suggested[10] in high-temperature superconductivity can be evaluated and the microscopic information about the electronic structure of the compounds obtained.

We have found that: (1) Under our experimental conditions, the maximum hydrogen uptakes in V_3Ga are $\sim$ 38 and $\sim$140 times those in V_3Ge and V_3Si, respectively; (2) a large T_c suppression occurs in V_3Ga and V_3Ge but not in V_3Si; and (3) the pressure coefficient of T_c of V_3Ga is independent of the H concentration. A hydride phase in V_3Ga is also suggested in the high H concentration region. The results will be discussed and the effects of hydrogenation and irradiation compared.

II. EXPERIMENTAL

The starting *A*15 compounds of V_3M with $M =$ Ga, Ge, and Si were prepared by arc melting the constituents in an argon atmosphere many times to enhance the homogeneity. For V_3Ga, the total weight loss was determined to be 0.8% after arc melting. This was attributed mainly to the loss of Ga, corresponding to a reduction of the quoted nominal value of 1 by 0.024. However, no weight loss was detected for V_3Ge and V_3Si. X-ray examinations revealed single phase in all samples investigated within our resolution ($\lesssim 5\%$). No metallographic analysis was made to determine the homogeneity of the samples. They were then annealed in vacuum at 750° C for 25 h prior to hydrogenation. The superconducting transition width was $\sim$0.05 K for all three unhydrogenated samples and the onset temperatures of the transition were 15.3, 6.1, and 16.1 K for V_3Ga, V_3Ge, and V_3Si, respectively. V_3MH_x were obtained by heating the V_3M up to 600° C for 12 h and then cooling slowly to room temperature in a hydrogen atmosphere with pressure up to 150 bar. A quartz chamber was used for pressure less than $\sim$11 bar and a stainless-steel chamber for higher pressure. Two other methods were also employed for preparing

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V_3SiH_x by dipping the V_3Si in a 50% HF or a 30% HNO_3 aqueous solution and by electrolytic charging. To determine the hydrogen concentration, V_3MH_x was heated at 450° C for 10 h in a small quartz tube connected to a 500-ml quartz container at room temperature. Both the quartz tube and container were evacuated prior to heating. The amount of hydrogen so desorbed was then measured with a mass spectrometer against three hydrogen calibrators with three different known pressures. The uncertainty of x in V_3MH_x was estimated at $\pm$ 10% of x. The x so determined represented the lower limit of hydrogen concentration, although the superconducting onset temperature accompanying with a broader transition ($\sim$0.5 K) was recovered after the hydrogen desorption.

The lattice parameter a_0 was determined with a Debye-Scherrer camera using the Cu $K\alpha$ radiation. The uncertainty in a_0 was obtained to be ± 0.001 Å by a $\cos^2\theta$ extrapolation. The superconducting transition was detected by a standard ac inductance bridge operating at 28 Hz. The temperature was determined by a Ge thermometer. High-pressure measurements were carried out by a self-clamp technique[11] with a 1:1 n-pentane and isoamyl alcohol solution. The pressure at low temperature was determined by a superconducting Pb manometer.

III. RESULTS

Within our experimental ranges, the amount of hydrogen in V_3MH_x was found to increase with the temperature and the hydrogen pressure at which hydrogenation took place. The maximum x's in V_3MH_x obtained by heating V_3M at 580° C under 150 bar of H_2 atmosphere (our maximum temperature and pressure for hydrogenation) for M = Ga, Ge, and Si are 1.96, 0.054, and 0.014 corresponding to 32.9, 1.39, and 0.35 at.%, respectively. In general, the introduction of hydrogen to V_3M suppresses T_c and enlarges a_0. No change is evident in the basic $A15$ symmetry in V_3MH_x to our maximum x.

In Fig. 1, T_c is shown as a function of both x and a_0 for V_3GaH_x, where the solid and dashed vertical bars represent the transition widths, respectively, during H charging and discharging, the upper horizontal bars the uncertainties in a_0 and the lower horizontal bars the uncertainties in x. As displayed in Fig. 1, for $x < 0.4$, T_c decreases rapidly and almost linearly at a rate of 0.7 K / [H] (at.%), with increasing x and a_0. For $x > 1.4$ no superconductivity was detected down to 1.5 K. We found it extremely difficult to obtain samples with $0.4 < x < 1.4$ on H_2 charging. However, a sample with a $T_c = 2.6$ K and $x = 1.04$ was prepared during H_2 discharging by heating the $V_3GaH_{1.92}$ compound in vacuum at $\sim$100° C for 0.5 h. No effort of ours succeeded both during

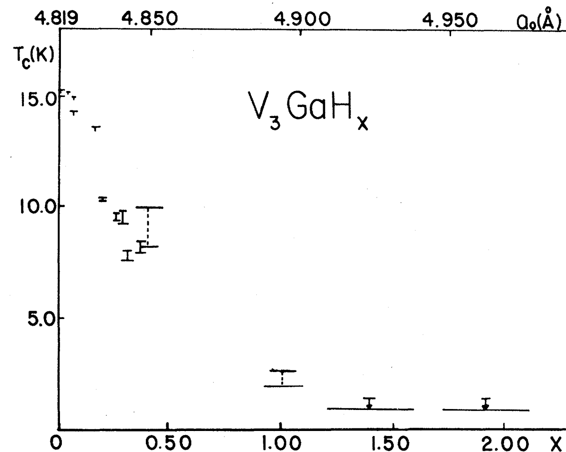

FIG. 1. The x and a_0 dependences of the T_c of V_3GaH_x during H charging (solid vertical bars) and H discharging (dashed vertical bars). The upper horizontal bar represents the uncertainty in a_0, the lower one the uncertainty in x. The arrow stands for the absence of superconductivity above the temperature indicated.

H_2 charging and discharging to achieve $0.4 < x < 1.04$. The x-ray diffraction patterns of the V_3GaH_x do not exhibit any line broadening, suggesting the homogeneity of the hydrogenation. The increase in the superconducting width may be attributed to the local strain in the sample due to the H_2-induced lattice expansion, since a nonhydrostatic pressure is known to have a large detrimental effect[12] on the T_c of high-T_c $A15$ compounds. The a_0 was found to vary linearly with x as shown in Fig. 2, from which the gap for $0.4 < x < 1.04$ was clearly evident. The vertical and horizontal bars stand for the uncertainties in a_0 and x, respectively. The x and a_0

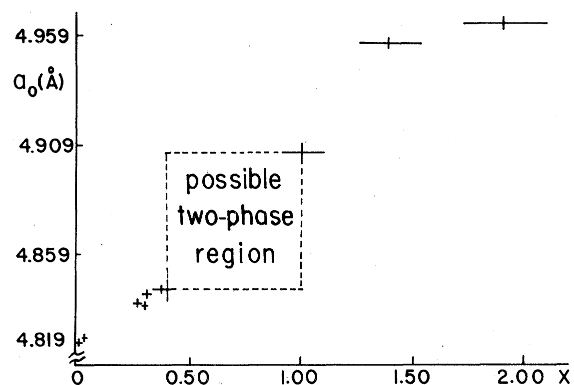

FIG. 2. a_0 vs x for V_3GaH_x.

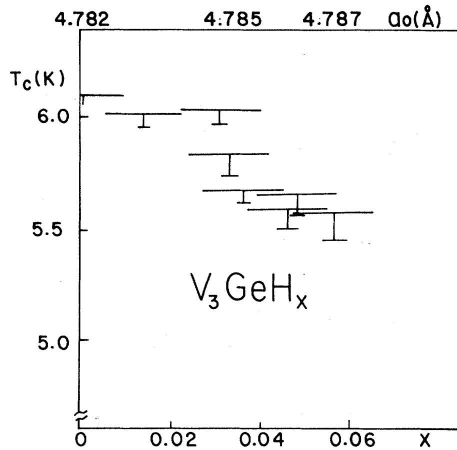

FIG. 3. The x and a_0 dependences of the T_c of V_3GeH_x. The same notation as that in Fig. 1 is used.

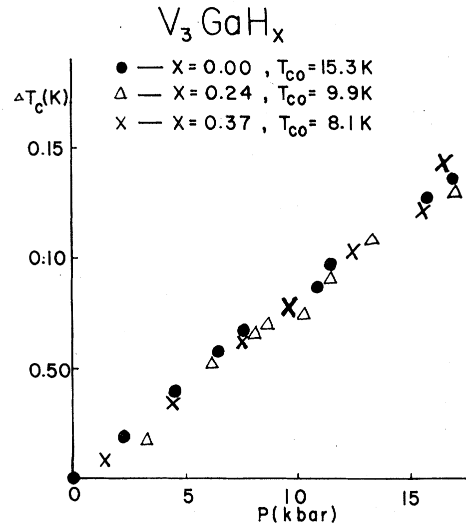

FIG. 4. The pressure-induced shifts of T_c in V_3GaH_x as a function of pressure.

dependencies of T_c for V_3GeH_x are given in Fig. 3, where the notations used are similar to those in Fig. 1. For the case of V_3SiH_x, no shift of T_c beyond our experimental resolution of ± 0.005 K was detected at the maximum x of 0.014 together with an a_0 expansion of 0.002 Å.

The pressure effects on the T_c of three V_3GaH_x were determined up to 18 kbar. At atmospheric pressure, their T_c's are, respectively, 15.3, 9.9, and 8.1 K for $x = 0$, 0.24, and 0.37. The pressure-induced shifts in T_c are shown in Fig. 4 as a function of pressure. It is clear to see that pressure enhances the T_c at a rate of 0.81×10^{-5} K bar^{-1} for all samples investigated, independent of x.

IV. DISCUSSION

For later comparison, we have summarized in Table I some data on the hydrogenated and irradiated V_3Ga, V_3Ge, V_3Si, Nb_3Ge, and Nb_3Sn.

In spite of the close similarity among V_3Ga, V_3Ge, and V_3Si, there exists a large variation in the amounts of hydrogen that can dissolve in these compounds under the same conditions. For instance, the maximum x's obtained in V_3GaH_x are ~38 and ~140 times those in V_3GeH_x and V_3SiH_x, respectively, under the most favorable conditions of ours. Therefore, the susceptibility S of these compounds to hydrogenation decreases in the order of V_3Ga, V_3Ge, and V_3Si. Earlier, it was noticed[8] that hydrogenation took place much more easily in Nb_3Ge than in Nb_3Sn. As shown in Table I we find that such a trend of S variation is also followed by the rate of percentage increase of a_0 due to hydrogenation in both the V- and Nb-based systems; i.e., S increases as $\Delta a_0/a_0$ per at. % of H absorbed increases. In other words, it is easier to dissolve an H atom in an $A15$ compound when the lattice of this compound opens

TABLE I. Some information about the hydrogenated and irradiated V_3Ga, V_3Ge, V_3Si, Nb_3Ge, and Nb_3Sn. * stands for T_c for unhydrogenated samples.

	V_3Ga	V_3Ge	V_3Si	Nb_3Ge	Nb_3Sn
T_{c0}^* (K)	15.3[a]	6.1[a]	16.1[a]	22	18
a_0(Å)	4.819[a]	4.782[a]	4.723[a]	5.133[b]	5.290[c]
$\Delta T/[H]$(K/[H](at.%))	0.7[a]	0.4[a]	<0.01[a]	0.6[b]	0.5[c]
$\Delta a/a_0[H]$(%/[H](at.%))	0.091[a]	0.072[a]	0.012[a]	0.108[b]	0.046[c]
$\Delta a_0/a_0\alpha$(%/$10^{18}\alpha$(cm^{-2}))	. . .	>0.57[d]	0.57[d]	10.0[d]	4.29[d]
$\Delta a_0/a_0 n$(%/$10^{18}n$(cm^{-2}))	. . .	. . .	. . .	0.034[e]	0.019[e]

[a] Present work. [b] Reference 8. [c] Reference 4. [d] Reference 3. [e] Reference 2.

up more readily to accomodate the large H atom. This seems to be consistent with the observation that S is larger for V_3M with larger a_0 as shown in Table I. Unfortunately, such a S-a_0 correlation is no longer valid for Nb_3Ge and Nb_3Sn. Since the tetrahedral sites are less closely packed than the octahedral sites in an $A15$ structure, the former are more likely to be occupied by the dissolved H atoms. It is also clear from Table I that the a_0 increase rate induced by α or n irradiation also varies in the same fashion as that induced by hydrogenation. In view of the metallurgical difficulties involved in preparing a stoichiometry and defect free V_3Ga or Nb_3Ge, the large susceptibility of hydrogenation or irradiation induced defect formation may be associated with the high metastability of the compounds. Whether the large S is caused by the enhanced trapping[8] of H or by the inherent defects of a metastable compound is yet to be proved. In this respect, it should be noted that the rate of n-induced T_c degradation was previously observed to increase continuously in V_3Ga_x (Ref. 13) for x varying from <1 to >1, but to pass a maximum[1] in Nb_3Al_x and Nb_3Pt_x at $x=1$. No correlation of S with T_c or a_0 of the unhydrogenated $A15$ compounds was found. The extreme difficulty to obtain x between 0.4 and 1.4 in V_3GaH_x (see Fig. 2) leads us to the suggestion of the possible existence of a hydride phase.

As shown in Table I the rate of T_c suppression by hydrogen at the low-concentration region is about the same for the hydrogenated V_3Ga, V_3Ge, Nb_3Ge, and Nb_3Sn ranging from 0.4 to 0.7 K/[H] (at.%). However, no T_c shift larger than $\pm$ 0.005 K was detected in V_3SiH_x. While it is true that the maximum x in V_3SiH_x is only 0.014 (corresponding to 0.35 at.%), a T_c reduction of 0.14 K would have been expected, even based on a rate of 0.4 K/[H] (at.%). Our observation is consistent with the earlier suggestion[7] that the T_c of a relatively stable and defect free V_3Si is rather insensitive to the initial drop in the density of states at the Fermi energy due to the shortening of the electron lifetime resulting from the electron-imperfection scattering. A specific-heat experiment to determine if the electron density of states of $V_3SiH_{0.014}$ is indeed drastically suppressed with its T_c unaffected is currently planned.

Studies on defected $A15$ high-T_c compounds except Mo_3Ge (Ref. 14), which has a very low density of states, have revealed two simple universal T_c-a_0(Ref. 15) and T_c-RR^3[resistivity ratio (RR)] correlations; i.e., T_c increases with a_0 decrease and RR increase, independent of the origin of defects which causes the changes in a_0 and RR. According to these correlations, pressure should always enhance T_c and the rate of T_c enhancement should be larger for samples with lower T_c. However, study[16] on the sputtered Nb-Ge thin films with a wide range of T_c, caused by varying the deposition conditions of the films, yields results in complete defiance of the predictions; i.e., pressure always suppresses T_c at a decreasing rate with T_c decrease. Although we have observed in the present investigation that pressure always enhances T_c of V_3GaH_x, the rate of T_c enhancement remains unexpectedly constant, independent of x (see Fig. 4). This confirms the suggestion[16] that defects do not affect T_c through the accompanying volume expansion. It also demonstrates that, in spite of the insensitivity of the T_c degradation to the origin of imperfections, differentiation does exist between imperfections introduced by hydrogenation and variation in sample preparation conditions. In fact, insofar as the annealing recovery of T_c is concerned, the T_c degradation of the hydrogenated and irradiated compounds is reversible, whereas that of the compounds prepared under conditions other than optimum are not. For instance, one has not been able to raise the low T_c of a defected Nb_3Ge sample prepared under nonoptimal conditions. To understand such difference is one of the most challenging problems in the study of high-T_c compounds. Further study on defected samples due to hydrogenation and irradiation will be very helpful. Preliminary investigation[17] on the near edge x-ray absorption of V_3GaH_x seems to indicate that, within the experimental resolution of a few eV, large electronic structure changes occur only in V sites but not in Ga sites.

V. CONCLUSION

We have studied the hydrogenation in V_3Ga, V_3Ge, and V_3Si. The susceptibility S to hydrogenation was found to decrease rapidly in the order of V_3Ga, V_3Ge, and V_3Si. At the same time, S increases with increasing rate of the a_0 expansion due to hydrogenation. The same is true for the hydrogenated Nb_3Ge and Nb_3Sn. The large S may be related to the high metastability of the compounds. The irradiation induced a_0-expansion rate varies with compounds in the same fashion as the hydrogenation induced rate of a_0 expansion. The results of this study also suggest the possible existence of a hydride phase of V_3GaH_x for $x \geq 1.4$.

Although hydrogen was found to rapidly suppress the T_c of V_3Ga and V_3Ge, no effect was detected in V_3Si. This is consistent with the suggestion that T_c of a nearly perfect V_3Si depends less sensitively on the electron density of states at the Fermi energy. Specific-heat measurements on V_3SiH_x are planned.

The pressure was found to enhance the T_c of V_3GaH_x at a constant rate, independent of x although the accompanying T_c ranges from 8.1 to 15.3 K. The reason is still unknown. However, comparison of the present results with those on the Nb-Ge sputtered thin films suggests that defects due to hydrogenation and irradiation may play a different role in high-

temperature superconductivity from those due to the variation in sample preparation conditions. A near edge x-ray-absorption investigation to assess the role of hydrogen in V_3Ga is currently under way. Preliminary results indicate that changes occur only at the V sites.

ACKNOWLEDGMENTS

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