

Influence of Hydrogenation on Electrical Conductivity of Vanadium Dioxide Thin Films

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Abstract—The influence of hydrogenation on electrical conductivity of vanadium dioxide thin films has been investigated. It has been shown using measurements of the electrical conductivity that the hydrogenation of vanadium dioxide thin films leads to a decrease in the temperature of the phase transition from the tetragonal phase (with “metallic” conductivity) to the semiconducting monoclinic phase. It has been found that, upon doping of vanadium dioxide with hydrogen, the electrical conductivity of the monoclinic phase can increase by several orders of magnitude. Nonetheless, the temperature dependence of the electrical conductivity of hydrogenated films exhibits a typical semiconducting behavior in the temperature range where the monoclinic phase is stable.

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1. INTRODUCTION

Single crystals of pure stoichiometric vanadium dioxide (VO_2) during cooling at temperatures below $T_c = 640$ K undergo a structural phase transition from the tetragonal phase to the monoclinic phase. This phase transition is initiated by the formation of chemical bonds between pairs of the neighboring vanadium ions and accompanied by a considerable (to 10^5) decrease in the electrical conductivity [1, 2]. Owing to this significant increase in the electrical resistivity due to the chemical localization of conduction electrons in the pairing of vanadium ions, the phase transformation occurring in vanadium dioxide can be considered as a metal–semiconductor phase transition. In our previous works [3, 4], we revealed and investigated an interesting phenomenon of hydrogen penetration into polycrystalline vanadium dioxide thin films in the case where these films were simply immersed in aqueous solutions of alcohols. It was shown that the rate of hydrogen penetration into the films very strongly depends on the state of vanadium dioxide. For the high-temperature (“metallic”) phase, the hydrogen penetration rate is one order of magnitude higher than that observed at the same temperature for the semiconducting monoclinic phase. In [3, 4], we also found that, under normal conditions, the hydrogenated vanadium dioxide is unstable. Hydrogen begins to leave the film as soon as it is removed from the solution, and the rate of dehydrogenation of the “metallic” tetragonal phase is substantially higher than the rate of dehydrogenation of the monoclinic phase. Nonetheless, it was noted in [3, 4] that, upon relatively rapid cooling of the film, the results of hydrogenation are retained to the liquid-nitrogen temperature.

In this work, we have investigated the temperature dependence of the electrical conductivity of hydrogenated vanadium dioxide.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The electrical conductivity of vanadium dioxide thin films was measured according to the standard four-point probe technique. Platinum contacts were deposited onto a fused silica (SiO_2) substrate by laser ablation in vacuum, and on the top of them, the VO_2 film was synthesized also by laser ablation of metallic vanadium in an oxygen atmosphere. The substrates had a thickness of ~ 0.4 mm, whereas the thickness of the synthesized films varied in the range 200–250 nm, which was three to four times larger than that used in [3, 4]. The thicker films in our present work were chosen in order to retain the maximum possible amount of hydrogen inside the films in the process of measurement of the electrical conductivity. On the one hand, the hydrogenation of these films required a more time, but, on the other hand, the release of hydrogen from the thick films also occurred for a longer time. When the “metallic” phase of vanadium dioxide was subjected to both hydrogenation and dehydrogenation, these times were approximately equal.

Moreover, the concentration profile of hydrogen in the film subjected to dehydrogenation could become such that part of the hydrogen would be blocked inside the film by its outer layer. Since the outer layer of the film is depleted in hydrogen, the hydrogen diffusion coefficient in this layer is significantly less than that in the heavily hydrogenated regions adjacent to the con-

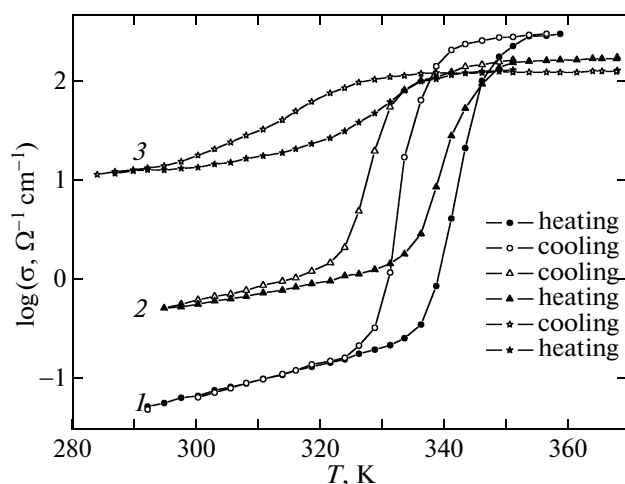


Fig. 1. Temperature dependences of the electrical conductivity of H_xVO_2 thin films: (1) $x = 0$, (2) $x \sim 0.012$, and (3) $x \sim 0.02$.

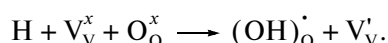
tacts. This means that different mobilities of protons can be accompanied by a specific kinetic autolocalization of hydrogen.

The films were hydrogenated by dipping the samples in an aqueous glycerol solution, which was preliminarily heated to temperatures in the range 370–390 K. The hydrogenation time did not exceed 15–30 min. As was done in [3, 4], the content of hydrogen (x) in the H_xVO_2 films was judged from the phase transition temperature.

The state of the studied material in the course of experiments was additionally controlled using the Raman scattering technique. The Raman spectra were recorded at room temperature on a HORIBA Jobin Yvon MRS 320 micro-Raman spectrometer with a resolution of better than 1 cm^{-1} .

3. RESULTS AND DISCUSSION

The penetration of hydrogen from an aqueous glycerol solution into vanadium dioxide is a result of the dehydrogenation of glycerol [3] on the surface of the film. The chemisorption of the formed hydrogen atoms is accompanied by the formation of OH^- ligands instead of the O^{2-} ligands in the crystal structure of vanadium dioxide, as well as by the formation of V^{3+} ions in the cation sublattice. In the Kröger–Wink notation, the reaction of the H radicals with VO_2 can be written in the form



This reaction implies that hydrogen in vanadium dioxide is a donor. It is worth noting that, as in [3, 4], the hydrogenated vanadium dioxide will be designated by the short formula H_xVO_2 . From the above reaction, it follows that the compound formed as a result of the

hydrogenation can also be described by the equivalent formula $VO_{2-x}(OH)_x$.

Figure 1 shows the temperature dependences of the electrical conductivity of vanadium dioxide thin films with different degrees of hydrogenation in the temperature range limited during cooling by room temperature. These dependences are characteristic of first-order phase transitions in solids. It can be seen from Fig. 1 that, in the phase transition temperature region, there is a hysteresis. As the hydrogen content increases, the phase transition temperature decreases, whereas the magnitude of the abrupt change observed in the electrical conductivity due to the phase transformation gradually decreases. It should be noted that, in [3], we observed a similar decrease in the magnitude of the abrupt change in the reflectance of vanadium dioxide films with increasing degree of hydrogenation.

The observed decrease in the phase transition, i.e., the broadening of the temperature region of stability of the tetragonal phase, is caused to a large extent by distortions of the crystal structure of vanadium dioxide. It is obvious that the replacement of a part (x) of the O^{2-} ligands with the OH^- ligands and the appearance of x ions V^{3+} instead of the V^{4+} ions inside the oxygen octahedra will lead to a noticeable distortion of the lattice. In this sense, the hydrogen embedded in the vanadium dioxide lattice can be considered as a source of the “internal” pressure which gives rise to elastic strains responsible for the decrease in the temperature of the phase equilibrium T_c . In [4], it was shown that the decrease in the temperature T_c occurs without regard to the particular (tetragonal or monoclinic) phase which is subjected to hydrogenation. This circumstance permitted us to observe the phase transition from the monoclinic phase to the tetragonal phase immediately at the hydrogenation temperature.

It should be noted here that the phase transition occurring in vanadium dioxide represents a martensitic transformation, which is very sensitive to elastic strains that are applied from the outside and arise in the course of the phase transition due to the difference (misfit) between the lattice parameters of the tetragonal and monoclinic phases. The role of these strains is especially significant in the case of thin films [5–8] and single microcrystals bound by the forces of adhesion to the substrate [9, 10]. Eventually, it is this circumstance that allows one to consider the structural transition in vanadium dioxide as a strain-driven phase transition [10].

An increase in the hydrogen content in the film leads to a gradual decrease in the difference between the electrical conductivities of the monoclinic and tetragonal phases due to the structural transformation. This difference slightly exceeds 10^3 in the initial polycrystalline film and decreases to one order of magnitude at a doping level $x \approx 0.02$. The decrease in the difference between the electrical conductivities is primarily associated with the increase in the electrical

conductivity of the monoclinic phase, because, as was noted above, the hydrogen embedded in the VO_2 lattice is a donor. At the same time, the electrical resistivity of the “metallic” tetragonal phase increases because of the increase in the structural disorder introduced as a result of the doping of the vanadium dioxide film with hydrogen.

We extrapolated the dependence of the difference in the electrical conductivity upon the phase transition in H_xVO_2 on the hydrogen content x . The extrapolation allows us to assume that, at $x \approx 0.04$, the phase transition can disappear and the “metallic” tetragonal phase will remain a stable phase in the entire temperature region under investigation. A similar result for nonstoichiometric single crystals V_{2-y}O_3 was observed in our previous work [11]. It was suggested that the decrease in the abrupt change of the electrical conductivity qualitatively indicates a decrease in the gain of a free energy of the crystal which is associated with the change in the electronic subsystem. Previously, according to the results obtained from the reflectance measurements [3], we reported on the suppression of the phase transition in vanadium dioxide films due to the hydrogenation. It was found that the increased (compared to the nonhydrogenated films) values of electrical conductivity and reflectance are observed down to 120 K.

It seems likely that, at a high hydrogen content x , the gain in the free energy, which is provided by the change in the electronic subsystem, has already not compensated for the increase in the elastic energy of the H_xVO_2 thin film upon the structural transition which is responsible for these changes. Qualitatively, this can be understood by considering the energy band diagram of vanadium dioxide [1]. During the transition from the metallic state to the semiconductor state, when every two neighboring vanadium ions approach each other, the σ bonds are formed between these ions and the lattice parameter is doubled, which, in turn, leads to a splitting of the narrow $d_{||}$ conduction band into two identical bands separated by an energy gap. Because the conduction band in the initial state was filled with exactly half, the lower $d_{||}$ band after splitting turns into the completely filled valence band, while the upper band remains empty. It is this circumstance that provides the gain in energy of the electronic subsystem upon the Peierls transition from the tetragonal phase to the insulating monoclinic phase. The displacement of the V^{4+} ions from the center of the oxygen octahedron leads to an increase in the overlap of the π orbitals of the vanadium and oxygen atoms and, accordingly, to an increase in the energy of the π^* band, which in the monoclinic configuration of VO_2 plays the role of a conduction band. Owing to the doping of the tetragonal phase, the electrons of the donors (H atoms) land in the $d_{||}$ conduction band; as a result, it becomes filled with more than half, and its splitting into two bands most likely has already been energeti-

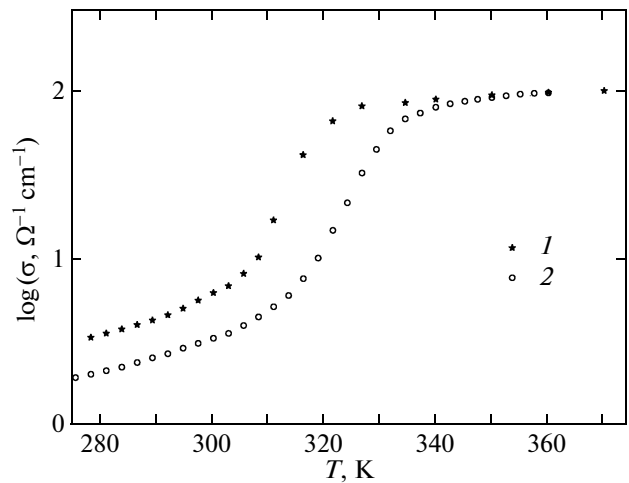


Fig. 2. Influence of the cooling rate (used in measurement of the temperature dependence of the electrical conductivity) of the hydrogenated vanadium dioxide thin film on the temperature dependence of the electrical conductivity: (1) cooling rate ~ 10 K/min and (2) cooling rate ~ 3 K/min. Hydrogenation was performed in glycerol at a temperature of 380 K for 10 min.

cally less favorable, because “extra” electrons migrate precisely into the π^* band. It is quite probable that, in a heavily doped vanadium dioxide, the energy gain due to the splitting of the $d_{||}$ band already does not exceed the consumption of the elastic energy required for the monoclinic distortion of the lattice. This leads to the complete suppression of the phase transition, and the “metallic” tetragonal phase becomes stable over the entire temperature range.

It cannot be also excluded, however, that the concentration of extrinsic electrons in the monoclinic phase (for $x \approx 0.04$, it is approximately equal to 10^{21} cm^{-3}) can exceed a critical value (conduction threshold) at which there occurs Mott transition to the metallic state. In the analysis of the energy band diagram of a heavily doped VO_2 , it is necessary to take into account the possibility of forming the impurity band, which will ensure “metallic” properties of H_xVO_2 down to very low temperatures.

The correct determination of the temperature region of stability of the “metallic” tetragonal phase is hampered by the instability of the hydrogen-doped vanadium dioxide. The duration of the most rapid measurements of the temperature dependence of the electrical conductivity in our experiment was several tens of minutes. During this time, the considerable part of the hydrogen atoms leaves the vanadium dioxide film. Figure 2 shows the temperature dependences of the electrical conductivity measured during cooling of the hydrogenated vanadium dioxide films at different rates. It can be seen from this figure that the rate of measurement affects both the temperature of transformation of the metallic phase into the semiconducting

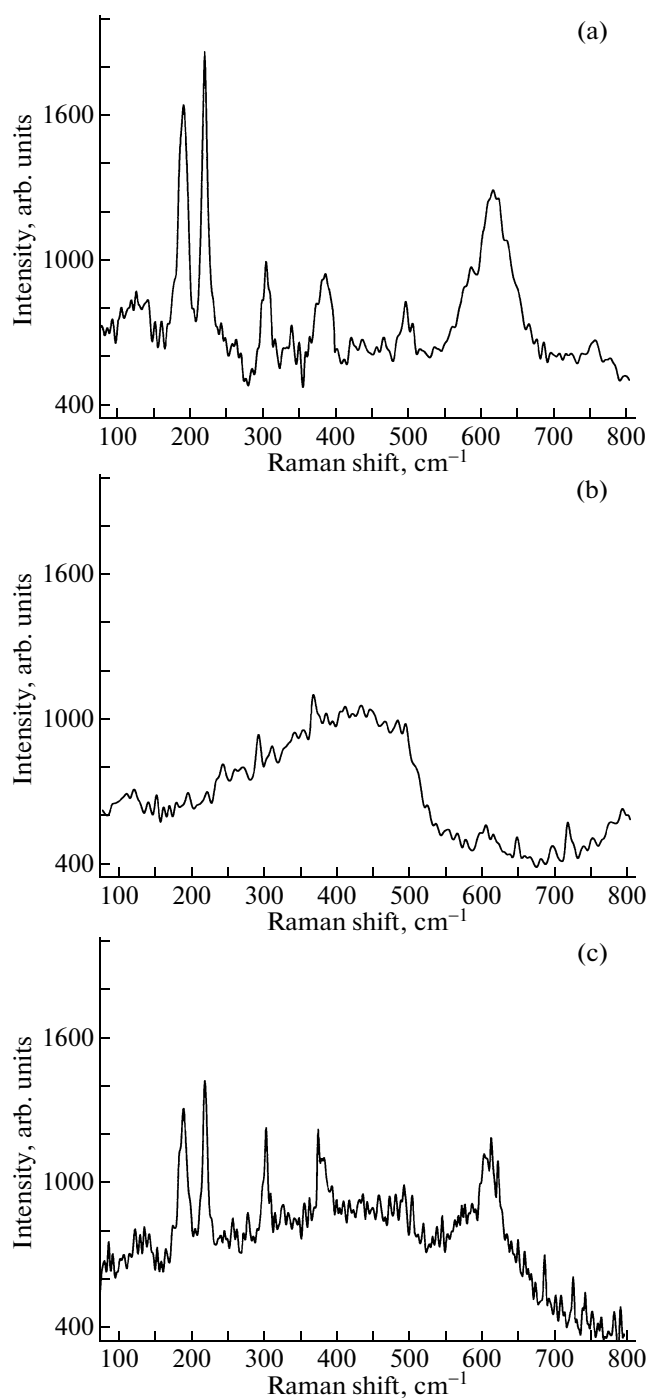


Fig. 3. Raman spectra of the polycrystalline vanadium dioxide film at room temperature: (a) the initial nonhydrogenated vanadium dioxide film, (b) the film immediately after hydrogenation in an aqueous solution of glycerol (for 30 min at 390 K), and (c) the same film after a short-term (~ 1 h) aging at room temperature.

phase and the change in the electrical conductivity, which accompanies this transformation. It should be noted that, during the measurement of the electrical conductivity, we could not stabilize the tetragonal

phase not only at low temperatures but also even at room temperature.

In [3], we showed that the rate of dehydrogenation of H_xVO_2 is determined by the amount of hydrogen incorporated into the film from the alcohol solution. The higher is the hydrogen content in the film, the larger is the hydrogen concentration gradient at the boundary between the surface of the film and the environment and the higher is the rate of release of hydrogen from vanadium dioxide after the removal of the sample from glycerol. Furthermore, the strength of the OH bond formed upon chemisorption of hydrogen by vanadium dioxide decreases with increasing concentration of free electrons [12]. In the tetragonal phase, the concentration of charge carriers is substantially higher than that in the insulating monoclinic phase. This leads to a decrease in the strength of the hydrogen–oxygen bond and causes a significant increase in the diffusion coefficient of hydrogen during the phase transition from the monoclinic phase to the “metallic” tetragonal phase [4]. In the light of the foregoing, it is obvious that the results presented in Figs. 1 and 2 characterize the H_xVO_2 films from which a part of the hydrogen released during measurements.

This point of view is also confirmed by the results obtained from the investigation of the Raman scattering spectra and presented in Fig. 3. All the spectral measurements were performed at room temperature. Figure 3b shows the Raman spectrum of a heavily hydrogenated ($x > 0.03$) vanadium dioxide film, which was recorded immediately after the completion of the hydrogenation performed in an aqueous solution of glycerol at a temperature of 390 K. A comparison of this spectrum with the initial spectrum (Fig. 3a) has demonstrated that all spectral bands, which are characteristic of the monoclinic phase of VO_2 , disappear after the hydrogenation, and the spectrum has the shape typical of the “metallic” tetragonal phase [1]. Figure 3c shows the evolution of the Raman spectrum due to the release of hydrogen from the film. After a short-term “ageing” of the sample in air at room temperature, this spectrum becomes, though not completely, but, to a large extent, identical to the initial spectrum. This is associated with the release of hydrogen from the surface layers of the film. At the same time, as judged from the reflectance of the film, the boundary between the hydrogenated and nonhydrogenated parts of the sample is still visible.

Thus, in the investigation of the optical and electrical properties of H_xVO_2 , we are faced with the fact that the uncontrolled release of hydrogen from thin films leads to a variability of the composition (gradient of x) across the thickness of the film. The concentration of hydrogen in internal regions of the film can significantly exceed the hydrogen concentration in the near-surface regions of the sample. We can imagine the case where the monoclinic phase resides near the surface, whereas the “metallic” tetragonal phase is located

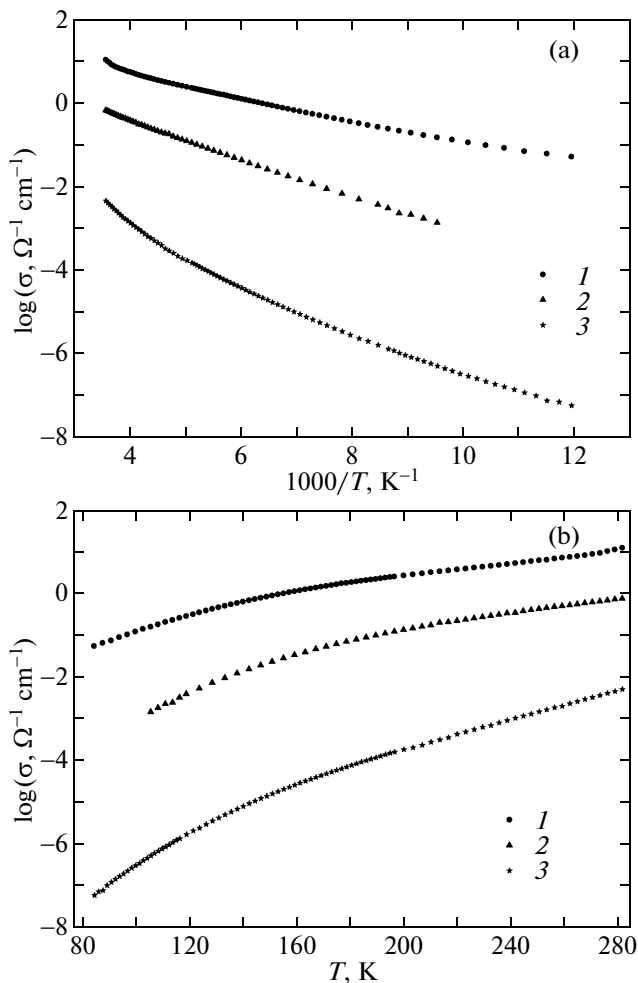


Fig. 4. Temperature dependences of the electrical conductivity of H_xVO_2 polycrystalline films (a) in the coordinates $\log \sigma \sim 1/T$ and (b) in the coordinates $\log \sigma \sim T$ for (1) $x \approx 0.03$, (2) $x \approx 0.01$, and (3) single crystals of pure vanadium dioxide.

inside the film as a result of the aforementioned kinetic autolocalization of hydrogen. The difficulties encountered in determining the diffusion profile of hydrogen in the hydrogenated vanadium dioxide were noted earlier in [4]. We should also say that the concentration profile will change directly during the measurement. Nonetheless, the results of the measurements of the electrical conductivity of these films are of considerable interest.

Figure 4 shows the temperature dependences of the electrical conductivity of the H_xVO_2 thin films in which the phase transition is suppressed only partially, so that the semiconducting monoclinic phase of vanadium dioxide should be stable in the chosen temperature range (77–280 K). The highest (available to us) level of hydrogen doping was achieved by a rapid (~3 min) cooling of the sample from the temperature of hydrogenation in glycerol (390 K) to the liquid-

nitrogen temperature. Dependences 3 shown in Figs. 4a and 4b were obtained during the subsequent heating of this sample. It is interesting to compare the dependences obtained for the hydrogenated films with the temperature dependence of the electrical conductivity of the single crystal of pure vanadium dioxide [13] (dependences 1 in Fig. 4). It can be seen from this comparison that the electrical conductivity of the H_xVO_2 thin films is substantially higher than that of the single crystal. The difference between the electrical conductivities increases with an increase in the hydrogen content x and a decrease in the temperature. At $T = 77$ K, for heavily doped samples, it reaches six orders of magnitude. Nonetheless, the semiconductor properties of the hydrogenated monoclinic phase are retained. The electrical conductivity of the doped samples significantly decreases with decreasing temperature. As in the case of conventional semiconductors, the slope of the temperature dependence $\log \sigma \sim 1/T$ (Fig. 4a) decreases with an increase in the level of hydrogen doping. As in the case of pure vanadium dioxide, in the temperature dependences plotted in the coordinates $\log \sigma \sim T$ (Fig. 4b), for the hydrogenated films below 160 K, we observe a noticeable deviation from the linear dependence and a crossover to the Arrhenius relationship $\log \sigma \sim 1/T$. Thus, as in the case of single crystals of pure vanadium dioxide [13], we can assume that the electrical conduction in the heavily doped monoclinic phase is provided by hopping of small-radius polarons.

4. CONCLUSIONS

Thus, the hydrogenation of polycrystalline vanadium dioxide thin films leads to a significant increase in the electrical conductivity of the semiconducting monoclinic phase. As the degree of hydrogenation increases, the metal–semiconductor phase transition in H_xVO_2 is suppressed and can completely disappear when the hydrogen content reaches $x \geq 0.03$. This assumption cannot be unambiguously proved or disproved because of the instability of the hydrogenated vanadium dioxide. The observed decrease in the difference between the electrical conductivities of the monoclinic and tetragonal phases raises the question regarding the nature of the phase transformation occurring in the hydrogenated vanadium dioxide: whether this phase transition is a metal–semiconductor phase transition or, as a result of hydrogenation, it turns into a phase transition between two “bad” metals (or two semiconductors) with different crystal structures.

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