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Quasiperiodic metallic multilayers: Growth and superconductivity

M. G. Karkut, J.-M. Triscone, D. Ariosa, and Ø. Fischer
Département de Physique de la Matière Condensée, Université de Genève, 1211 Genève 4, Switzerland
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We have magnetron-sputtered a series of Mo-V superlattices which have a quasiperiodic layering in the growth direction. We have used the Fibonacci series as the generating rule for the nearly periodic structures and have verified their structure using high-angle x-ray diffractometry. The superconducting transition temperatures slowly increase as a function of the quasiperiodic wavelength Λ_F, while the initial upper-critical-field slopes parallel to the films decrease with increasing wavelength, and the parallel upper-critical-field curves $H_{c2\parallel}$ display a two-dimensional behavior that is not consistent with current ideas about critical-field behavior in multilayers.

Since the discovery by Shechtman, Blech, Gratias, and Cahn[1] of the icosahedral symmetry of quench-condensed Al-Mn, quasicrystals and quasiperiodicity have occupied a preeminent position in the journal forum. Levine and Steinhardt[2] were the first to show theoretically that certain unallowed crystal symmetries are allowed quasicrystal symmetries. They analytically computed the diffraction patterns of an ideal three-dimensional (3D) quasicrystal, which they had built up from the 1D quasiperiodic Fibonacci lattice, and found the result closely related to the diffraction patterns of icosahedral Al-Mn. Merlin *et al.*[3] applied the ideas on 1D quasiperiodicity contained in Ref. 2 by making a 1D quasiperiodic GaAs-AlAs heterostructure. We, in turn, have taken Ref. 3 as a starting point, and have grown a series of quasiperiodic metallic superlattices with alternating layers of Mo and V, characterized their structure using x-ray diffractometry, and measured their superconducting critical temperatures and their perpendicular and parallel upper critical fields.

The 1D quasiperiodic state can be considered as intermediate between periodic states with extended electronic wave functions and random states with localized wave functions. It is believed that quasiperiodic systems can have states that are localized, extended, or neither localized nor extended.[4] It is not immediately clear how the effects of 1D quasiperiodicity should manifest themselves experimentally through, for instance, superconductivity, but the notion that 1D quasiperiodicity may be studied using multilayers is potentially very rich and has advantages over naturally occurring systems. Multilayers can be used as model systems in which it is possible to systematically study 1D quasiperiodicity by varying the constituents involved, the layer dimensions, and even the type of quasiperiodic pattern. By making metallic multilayers with quasiperiodic layering, one now has the potential to study the effects of aperiodicity on a wide variety of problems which may also lead to some insight into the behavior of the growing number of three-dimensional quasicrystals.

We previously reported[5] the epitaxial growth of periodic Mo-V superlattices. We chose Mo-V as our introduction to quasiperiodically layered systems because of our experience with this system. The samples produced for this study were magnetron sputtered under the same conditions we used to make periodic multilayers of Mo-V. The base pressure of the vacuum system was better than 4×10^{-9} Torr and the working pressure of flowing argon was 10 mTorr. The sputtering rate was 2.5 Å/sec and the (11$\bar{2}$0)-oriented Al_2O_3 substrates were held at a temperature of $\sim$700 °C during deposition so that optimum layering[5] could occur. We used a step motor driven by a minicomputer to position the substrates under the designated V or Mo target for the necessary amount of time. Mo was always the first and last element deposited and the samples ranged in total thickness from $\sim$2000 to $\sim$5500 Å. Each sample contained at least 60 alternating layers of Mo and V.

The quasiperiodic sequences were constructed using approximately the scheme one finds in Ref. 3. By starting with two buildings blocks A and B, each composed of Mo and V to ensure that a Mo layer always abuts a V layer and vice versa, one can construct, using a generating rule, a string of A's and B's that form an aperiodic sequence. We have used the Fibonacci sequence where an nth-order string of A's and B's is composed of the strings from the two previous orders. This is illustrated in Fig. 1, along

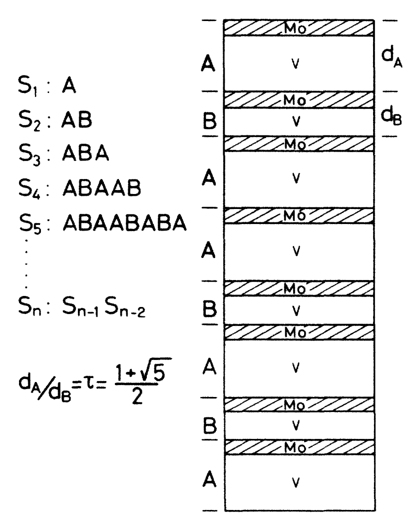

FIG. 1. Schematic diagram of a section of an ideal quasiperiodic (Fibonacci) superlattice along with the generating sequence.

TABLE I. Structural and electronic parameters of four of the samples.

Sample	Λ_F (Å)	Block A x Å Mo y Å V	Block B x Å Mo z Å V	Total thickness (Å)	T_c (K)	$\xi_\parallel(0)$[a] (Å)	$\xi_\perp(0)$[a] (Å)
Mo-V, No. 1	163	15 58	15 30	2000	2.39	235	127
Mo-V, No. 2	220	20 78	20 40	2600	2.94	245	93
Mo-V, No. 3	340	31 121	31 62	4160	3.30	231	89
Mo-V, No. 4	692	64 246	64 128	4110	3.68	223	84

[a]The coherence lengths are calculated from Eq. (1) and by extrapolating the $H_{c2}(T)$ data to 0 K.

with an idealized section[6] of an Mo-V Fibonacci multilayer. The blocks A and B consist of x Å of Mo-y Å of V and x Å of Mo-z Å of V, respectively. The ratio of $d_A/d_B=(x+y)/(x+z)=\tau$, and the ratio y/z is 2. This means that all samples have the same ratio of vanadium to molybdenum, which is a prerequisite for studying the superconducting properties as a function of wavelength. The thicknesses of blocks A and B are in the ratio of the golden mean τ, i.e., $d_A/d_B=(1+\sqrt{5})/2=\tau$, because this, along with the generating rule, makes the sequence self-similar. The quasiperiodic wavelength $\Lambda_F=\tau d_A+d_B$ is an average of the relative thicknesses of blocks A and B. The sequence is constructed so that there are τ times as many blocks of A than B. Table I lists four of the samples with some relevant structural and electronic parameters.

Figure 2 shows high-angle x-ray diffractograms of two samples with wavelengths of 163 and 340 Å. We have used a powder diffractometer in the θ-2θ geometry with Cu $K\alpha$ radiation. The satellite peaks around the main peaks can all be indexed using the numerically generated[3] formula $\Delta k=(2\pi/\Lambda_F)n\tau^p$, where Λ_F is the quasiperiodic wavelength, τ the golden mean, and n and p are integers. The scattering vector is $k=4\pi\sin\theta/\lambda_x$, where λ_x is the x-ray wavelength, and Δk is the difference in k from a satellite to the main peak. The main peak, indicated in Fig. 2, is the diffracted signal produced by the weighted average of the Mo and V layer spacings. Recall that for a *periodic* superlattice the distance between successive peaks is approximately constant and inversely related to the wavelength Λ_P, and is given[7] by $\Lambda_P=\lambda_x/2(\sin\theta_{i+1}-\sin\theta_i)$. This is no longer true for the quasiperiodic sequence because the situation is one where the peaks occur in a geometric progression with τ as the common ratio. The widths of the peaks also provide a lower limit on the crystalline coherence in the growth direction. Using the Scherrer formula[8] and taking into account the instrumental broadening, we determine a coherence of at least 400 Å for the samples presented in this work.

We measured the superconducting transition temperatures and the upper critical fields using a four-point ac resistance technique, with the 50% point of the resistive transition defining the critical temperatures. The transition widths in zero field range from 0.25 to 0.38 K and change only slightly in the presence of an applied field. The character of $H_{c2}(T)$ for the samples presented here is practically independent of the definition of H_{c2}. The T_c's of individual 3000-Å films of V and Mo on Al_2O_3 are 4.82

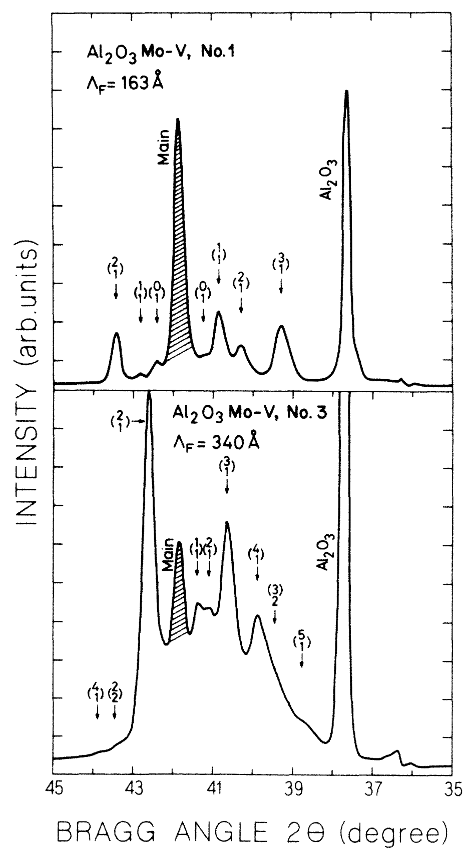

FIG. 2. High-angle diffractograms of two Fibonacci superlattices. The top number in the parentheses refers to p, the bottom to n, as discussed in the text.

and 0.62 K, respectively. We have measured the T_c's of nine Fibonacci multilayers with wavelengths between 135 and 692 Å. We observe that as the wavelength decreases from 692 to ~ 300 Å, T_c decreases slowly, and below 300 Å, T_c begins to fall more rapidly. The high-Λ_F T_c's would seem to be generally consistent with the proximity effect, whereas the low-Λ_F behavior could be the advent of the very abrupt drop in T_c that we observe[5] for periodic Mo-V samples.

In Fig. 3 we present the upper critical magnetic fields $H_{c2}(T)$ for orientations both parallel and perpendicular to the film of four Fibonacci samples. The perpendicular critical fields have a straight-line behavior which is what one, in principle, would expect for this orientation. For magnetic fields parallel to the layers, however, the slope of H_{c2} near T_c decreases with increasing wavelength. $-(dH_{c2}/dT)_{T_c}$ varies from an essentially infinite value for $\Lambda = 163$ Å to ~ 8 kG/K for $\Lambda = 692$ Å. As the wavelength increases, the curvature of $H_{c2\parallel}(T)$ near T_c goes from two-dimensional behavior, where $H_{c2\parallel}(T) \sim (1-T/T_c)^{1/2}$, to more three-dimensional-like behavior, where $H_{c2\parallel}(T) \sim (1-T/T_c)$. It is well established[9] that parallel upper critical fields in multilayers can exhibit 3D or 2D behavior depending on the thickness of the layers. Using anisotropic Ginzburg-Landau theory,[10] one can write the upper critical fields in terms of parallel and perpendicular coherence lengths $\xi_\parallel(T)$ and $\xi_\perp(T)$ as

$$\begin{aligned} H_{c2\parallel}(T) &= \phi_0/2\pi\xi_\parallel(T)\xi_\perp(T) \ , \\ H_{c2\perp}(T) &= \phi_0/2\pi\xi_\parallel(T)^2 \ , \end{aligned} \tag{1}$$

where ϕ_0 is the flux quantum. When the perpendicular coherence length $\xi_\perp(T)$ is much larger than the normal-metal[11] thickness, the superconducting layers are coupled, and 3D behavior is expected. When $\xi_\perp(T)$ is much less than the normal-metal thickness the superconducting layers are decoupled and the $H_{c2\parallel}(T)$ comportment depends upon the thickness of the individual superconducting layers. The experimental observation of dimensional crossover in, for instance, Nb-Cu multilayers[12] occurs when $\xi_\perp(T)$ is approximately equal to the separation of the superconducting layers. In a theory of the upper critical fields of superconducting superlattices developed by Tachiki and Takahashi,[13] one is in the 3D regime when the distance separating the superconducting layers is less than the coherence length $\xi(0) = [\phi_0/2\pi H_{c2}(0)]^{1/2}$, where $H_{c2}(0)$ is the zero temperature upper critical field of the bulk superconductor. The parallel field behavior for the samples presented is completely at odds with what we have just described. Because the $\Lambda_F = 163$ Å sample has $\xi_\perp(T=0) = 127$ Å and only 15-Å Mo layers separating the superconducting V layers, one would expect to see coupled, three-dimensional, linear-in-T behavior for its parallel upper critical field. Indeed, this is what we do see for a *periodic*, $\Lambda = 70$ Å, Mo-V superlattice, where the ratio of Mo to V is 1:1. This is depicted by the solid line in Fig. 3(a) and highlights the unusual nature of the $H_{c2\parallel}(T)$ curves. We observe the same $H_{c2}(T)$ behavior for two separate $\Lambda_F = 163$ Å samples: one with a total thickness of 2000 Å, the other with 3500 Å. The additional 1500 Å on

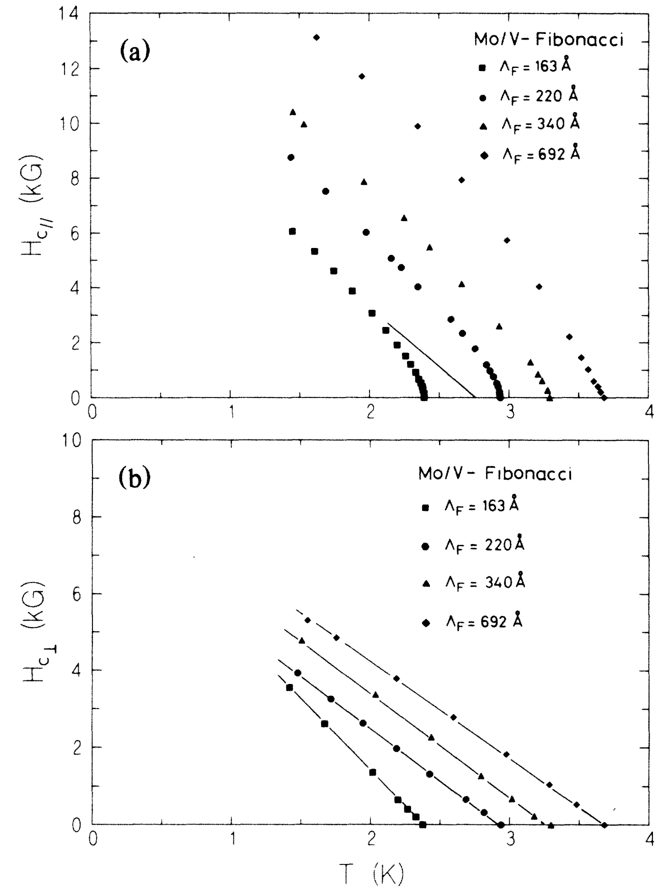

FIG. 3. Parallel and perpendicular upper critical magnetic fields of four quasiperiodic Mo-V superlattices. The solid line in (a) depicts the parallel upper-critical-field behavior of a 70 Å periodic Mo-V superlattice whose ratio of Mo to V is 1:1.

the second $\Lambda_F = 163$ Å sample, and the similarity of the $H_{c2\parallel(T)}$ curves, indicate that the manner of layering, if it is the cause of the $H_{c2\parallel}$ behavior, is already effective after 60 alternating layers of Mo and V.

We hesitate to ascribe this parallel field behavior to quasiperiodicity. From an experimental point of view we have not yet made a rigorous comparison with multilayers consisting of some periodic arrangement of the blocks *A* and *B*. One cannot rule out the still interesting possibility that it is the multiple layering produced by these building blocks that is the cause of the 2D-like curves. Also, from a theoretical point of view, it is not clear how quasiperiodicity will affect superconductivity. Our samples could be described as behaving as if the superconducting state is localized on a scale that is small compared to the total thickness of the sample and large compared to the individual layer thicknesses. Another aspect to consider in a Fibonacci superlattice is the flux structure. Does it form a regular lattice or does the quasiperiodicity impose itself to bring about something more exotic? Whatever the explanation, it seems that quasiperiodic superlattices should be capable of providing a basis for much interesting physics.

[1]D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2]D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984).

[3]R. Merlin, K. Bajema, Roy Clarke, F.-Y. Juang, and P. K. Bhattacharya, Phys. Rev. Lett. **55**, 1768 (1984).

[4]See, for example, S. Ostlund and R. Pandit, Phys. Rev. B **29**, 1394 (1984), and references therein.

[5]M. G. Karkut, D. Ariosa, J.-M. Triscone, and Ø. Fischer, Phys. Rev. B **32**, 4800 (1985); M. G. Karkut, J.-M. Triscone, D. Ariosa, and Ø. Fischer, Physica B **135**, 182 (1985).

[6]A real Mo-V multilayer will have interfacial layers on the order of 8 Å thick. A study of these interfacial layers and lattice strain and their effect on T_c in periodic Mo-V multilayers will be the subject of a future publication.

[7]I. K. Schuller, Phys. Rev. Lett. **44**, 1597 (1980).

[8]See, for example, B. D. Cullity, *Elements of X-Ray Diffraction* (Addison-Wesley, Reading, 1967).

[9]For a discussion of H_{c2} in layered superconductors, see S. T. Ruggiero and M. R. Beasley, in *Synthetic Modulated Structures,* edited by L. Chang and B. C. Giessen (Academic, New York, 1984).

[10]W. Lawrence and S. Doniach, in *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto,* edited by Eizo Kanda (Academic, Tokyo, 1971), p. 361.

[11]To simplify terminology we will call V (T_c = 4.82 K) the superconductor and Mo (T_c = 0.62 K) the normal metal.

[12]C. S. L. Chun, G. G. Zheng, J. L. Vicent, and I. K. Schuller, Phys. Rev. B **29**, 4915 (1984).

[13]M. Tachiki and S. Takahashi, Physica B **135**, 178 (1985).