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STRUCTURE AND PHYSICAL PROPERTIES OF SPUTTERED METALLIC SUPERLATTICES

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The technique of preparing metallic superlattices by sputtering is described as are the results of a calculation of the energy distribution of sputtered atoms. Structural studies by X-ray diffraction, Ion Mill Auger Electron Spectroscopy and Ion Mill Ion Scattering Spectroscopy all indicate well defined layer structure for the Nb/Cu system. The resistivity of Nb/Cu and Nb/Ti and the superconductivity of Nb/Cu are all found to be dependent upon the layered nature of the material.

1. Introduction

The study of two-dimensional metal physics has been dependent on the requirement of reliably preparing ultrathin (a few atomic planes thick) single films of metals. Due to contamination (e.g. oxidation) and because of inherent problems in the structure (aglomeration) and handling of such thin films, the physical properties of such films normally have to be measured in situ. This of course poses a large number of experimental difficulties and restricts the variety of physical properties that can be measured on identical samples. A possible alternative for the study of such two dimensional properties is the preparation of multilayered films. In this fashion it is possible to study the physical properties of thin metal films when they are separated by a suitable metal, semiconductor or insulator [1]. In addition, by varying the thickness of the "separator" it is feasible to investigate the transition to three-dimensional behavior. As we will show, many of the difficulties encountered using surface analysis techniques (i.e. Ion Mill Auger, Ion Scattering Spectroscopy, etc.) in characterizing thin metal films can be avoided by taking advantage of the long range order existent in metallic superlattices. We will describe here the structural and novel physical properties of the Nb/Cu and Nb/Ti metallic superlattices.

2. Preparation techniques

The materials described in the present paper have been prepared using a sputtering technique developed by us. Two high rate magnetron sputtering

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guns (see fig. 1) are placed in a high vacuum system (base pressure $\sim 8 \times 10^{-8}$ Torr). The sputtering guns are widely separated and shielded so as to avoid an overlap of the two sputtered particle beams. The rates are controlled by regulating the power to the guns and are monitored using crystal quartz oscillators. The single crystal substrates (90° Al_2O_3) are held on a rotating platform whose temperature is controlled using a non-contact temperature sensor, and a quartz lamp heater in a feedback loop. In this fashion the temperature of the substrate can be varied from room temperature to approximately 400°C with an accuracy of ±2°C. By properly regulating the sputtering rates and rotation speed of the platform, layers ranging in thickness from 2 Å to greater than 1 μm can reproducibly be prepared.

A possible advantage of sputtering over thermal deposition techniques is that control of the sputtering pressure (~ 10 mTorr of Argon) and the target to substrate distance allows control of the energy distribution of particles arriving at the substrate. Fig. 2 shows the calculated energy distribution of sputtered particles arriving at the substrate (in a realistic situation) for various target to substrate distances [2]. Notice that the farther the substrate is located from the target, the closer the final distribution is to the thermal distribution of the sputtering gas. A comparison (fig. 3) of the energy distribution of sputtered and evaporated Nb (for fixed rates at the substrate) shows the sputtered distribution to be sharper with a peak energy lower than that of evaporated

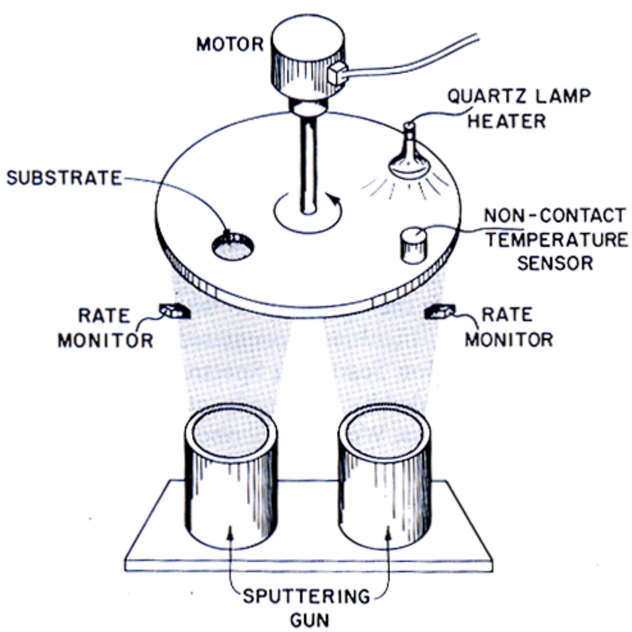
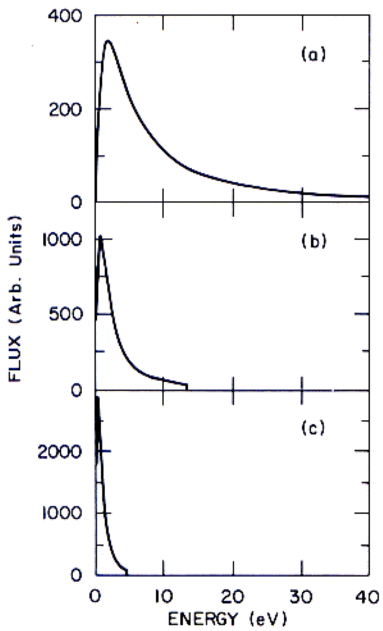


Fig. 1. Sputtering system used to prepare metallic superlattices.



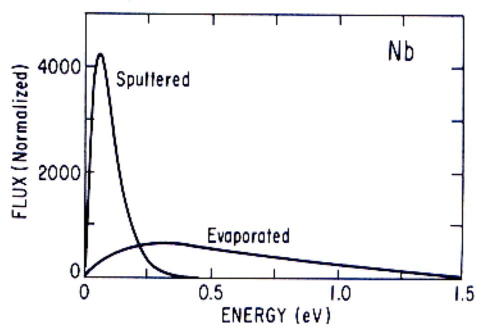


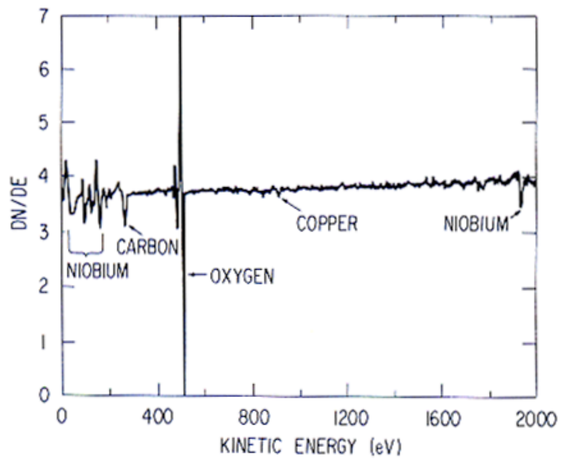
Fig. 2. Calculated Nb energy distributions as a function of distance from target with Ar gas pressure 10 mTorr. Distances are (a) 0 cm, (b) 3 cm, (c) 6 cm.

Fig. 3. Comparison of calculated energy distributions for sputtered and thermally evaporated Nb. Sputtering parameters are Ar gas at 10 mTorr and 550 K with a target voltage of 270 V. Evaporation temperature is 3600 K.

Nb. For the preparation of multilayers, it is important for the temperature of the substrate as well as the deposition rates to be high enough to promote epitaxy [3]. At the same time care should be taken that the energy of the particles arriving at the substrate is low enough to avoid disrupting the already formed layers. This is accomplished in a natural way using sputtering since the energy distribution and peak energy can be manipulated by changing sputtering pressures and substrate to target distance.

3. Structure

Multilayers of Nb and Cu were prepared using the technique described above. Ion Mill Auger Spectroscopy was performed to depth profile the chemical composition of the samples. Fig. 4 shows an Auger spectrum for the surface of a Nb(65 Å)/Cu(65 Å) multilayer. The spectrum indicates that the



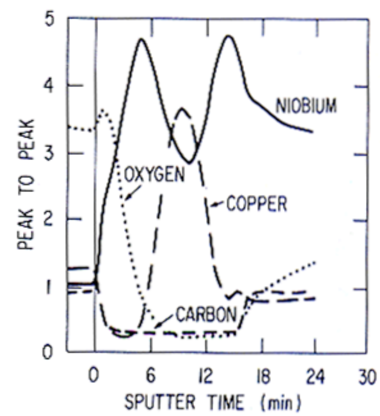


Fig. 4. Auger electron spectra for the surface of a Nb(65 Å)/Cu(65 Å) sample.

Fig. 5. Dependence of peak to peak Auger amplitude as a function of ion milling time (distance into sample) for a Nb(65 Å)/Cu(65 Å) sample.

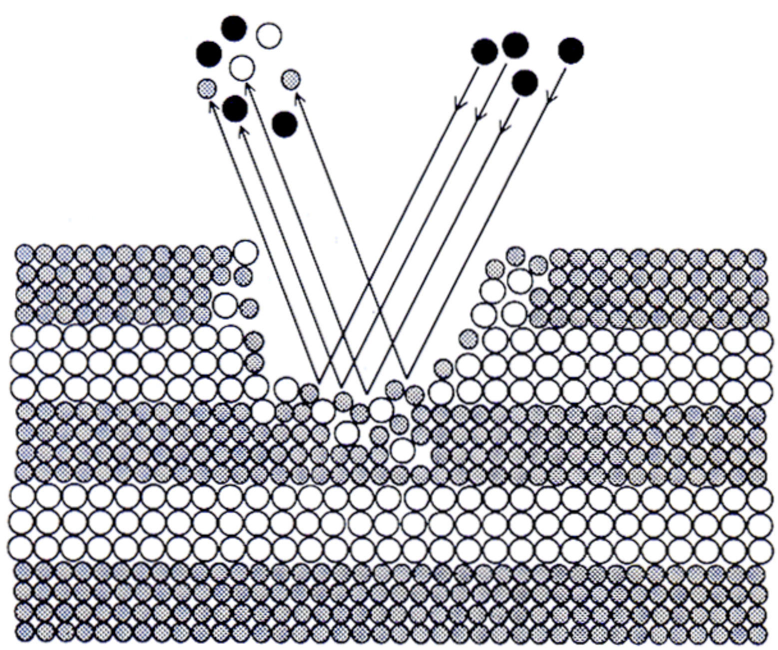
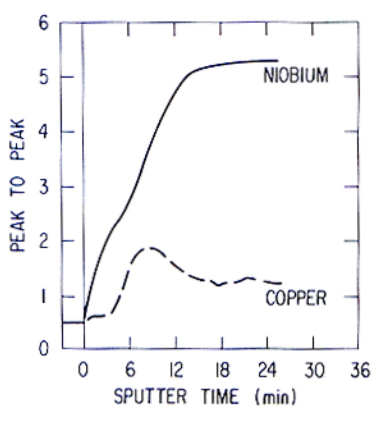


Fig. 6. Schematic representation of intermixing and cratering caused by process of ion milling.

surface layer is Nb and that the surface of the sample is considerably contaminated by oxygen and carbon. The sample was subsequently ion milled using 1 keV Ar ions in order to obtain a depth profile for niobium, copper, oxygen and carbon. This is shown in fig. 5. Within approximately ~ 20 Å (~ 3 min ion milling time) the carbon peak disappears, while after ~ 40 Å (~ 6 min) the oxygen peak is undetectable; indicating that only the surface of the sample is contaminated. It is interesting to note that after the ion milling is stopped (~ 16 min), the surface rapidly becomes recontaminated even at the low ambient pressure (~ 1×10^{-9} Torr). The copper and niobium peaks oscillate 180° out of phase as expected for a layered material.

It should be pointed out that the difficulty with Ion Mill Auger Spectroscopy is two-fold. The escape depth for the Auger electrons is in the most favorable case ~ 20 Å. Therefore the Auger signal indicates the chemical composition averaged over at least a 20 Å depth. In addition, ion milling causes significant intermixing of the layers (fig. 6) as well as cratering which tends to destroy the layered structure. In fact, because of this, ion mill Auger



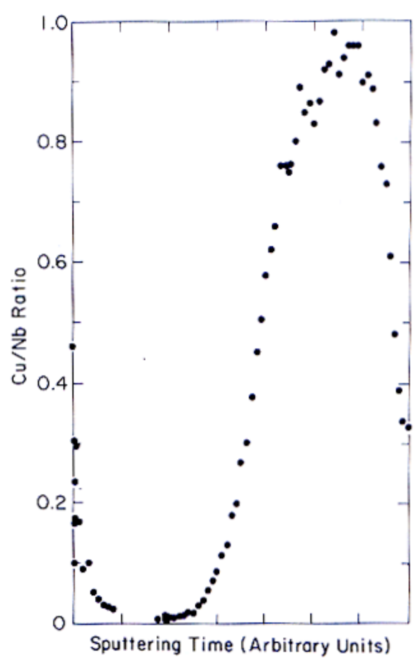


Fig. 7. Dependence of peak to peak Auger amplitude as a function of ion milling time (distance into sample) for a Nb(16.5 Å)/Cu(16.5 Å) sample.

Fig. 8. Ratio of Cu to Nb as derived from $^{20}Ne^{+}$ Ion Scattering Spectroscopy (ISS) as a function of ion milling time (distance into sample) for a Nb(65 Å)/Cu(65 Å) sample.

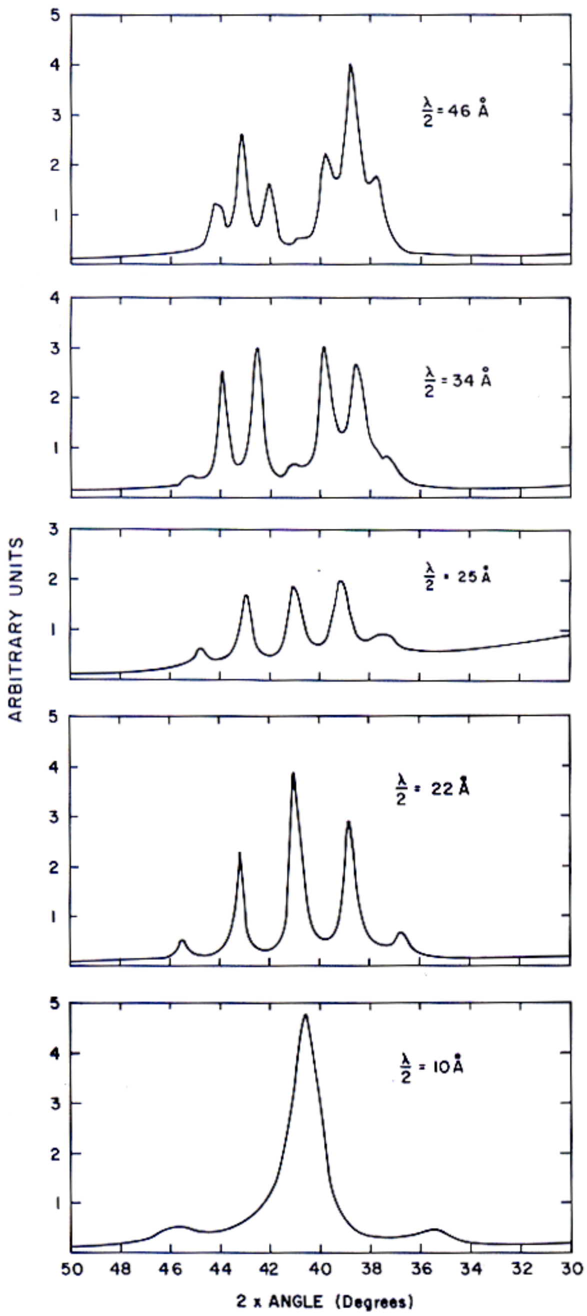


Fig. 9. Measured X-ray diffraction patterns for a sèries of Nb/Cu samples of different layer thicknesses (λ/2).

on a Nb(16.5 Å)/Cu(16.5 Å) sample, known from X-ray diffraction studies to be well layered, shows the first and barely a second oscillation in the Cu signal and only a weak shoulder on the Nb signal (fig. 7). Ion Scattering Spectroscopy (ISS) has also been performed in order to obviate the finite escape depth problem inherent in the Auger measurements. Fig. 8 shows the Cu/Nb ratio as a function of ion milling time ($^{20}Ne^{+}$ ions at 1 keV energy) for the Nb(65 Å)/Cu(65 Å) sample. For the first two layers one observes 100% modulation, although after the second layer intermixing problems caused by the ion milling are again distorting the signal. The conclusions from these measurements are that the chemical composition of these materials is modulated but that ion milling techniques are not useful for layer thicknesses below ~ 40 Å.

To further study the structure we have performed standard θ–2θ X-ray scattering on a variety of Cu/Nb samples. Since the X-ray momentum transfer is perpendicular to the layers this measurement is sensitive to structural changes perpendicular to the layers. Fig. 9 shows the X-ray intensity versus 2θ and fig. 10 shows a one-dimensional model calculation assuming 100% modulation and no adjustable parameters [4]. The various peaks arise from the scattering by the superlattice planes and therefore the layer thickness ($\lambda/2$) is given by the simple formula

$$\lambda = \tfrac{1}{2}\lambda_x(\sin\theta_i - \sin\theta_{i+1})^{-1}, \qquad (1)$$

where λ_x is the X-ray wavelength and i and $i+1$ refer to adjacent diffraction

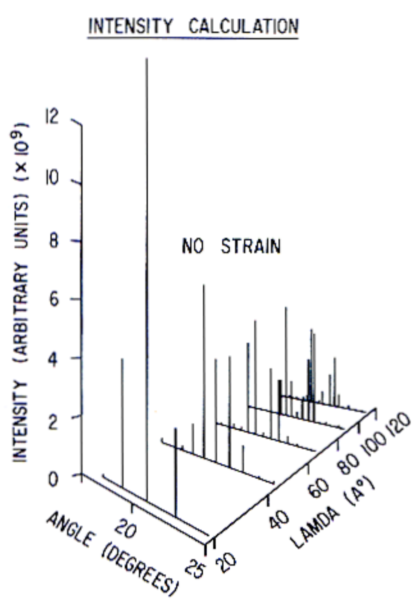


Fig. 10. Calculated X-ray diffraction patterns as a function of Nb and Cu layer thickness ($\lambda/2$).

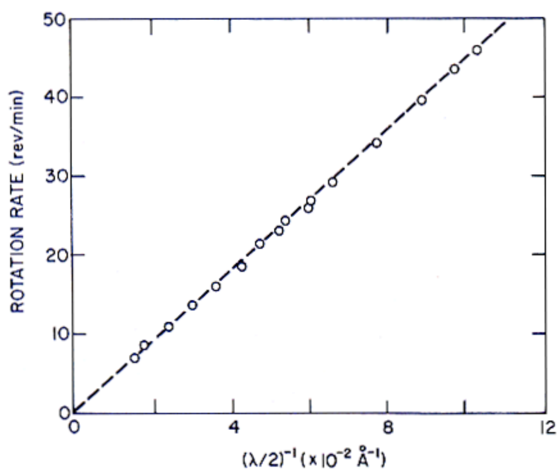


Fig. 11. Sample rotation rate versus inverse layer thickness as derived from X-ray diffraction measurements.

peaks. We should stress that the existence of a large number of superlattice reflections (up to eleven peaks) implies that the position of atomic planes perpendicular to the layers is correlated. As in any anisotropic system, several coherence lengths can be defined. In particular, the X-ray measurement described above indicates that the lower limit in the coherence of the Cu/Nb superlattice in the z direction (perpendicular to the layers) is ~ 10 superlattice wavelengths.

Fig. 10 shows that with no adjustable parameters one can obtain the qualitative behavior found experimentally. By assuming strains in the interfacial Cu or Nb layers, the intensity calculations agree to within $\sim 20\%$ with the experimentally measured intensities. An additional check on the correctness of this analysis is shown in fig. 11. For fixed preparation parameters (pressure, power, etc.) the layer thickness should only be dependent inversely on the speed of the rotating motor. This is found experimentally.

In addition, the total thickness of the sample (independently measured using a calibrated Sloan Dektac) is always within a few percent of the thickness calculated from the product of the individual layer thickness times the total number of revolutions.

4. Physical properties

The physical properties of metallic superlattices depend strongly on layer thickness. fig. 12 shows the dependence of in-plane resistivity for the Nb/Ti

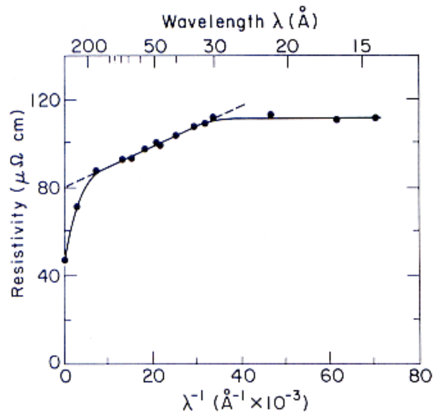


Fig. 12. In-plane resistivity versus inverse layer thickness for a series of Nb/Ti samples.

superlattice. For very thick layers the resistivity is given by the parallel resistance of the Nb and Ti layers. In the intermediate region shown in fig. 12 the resistivity is boundary scattering limited with a $1/\lambda$ dependence as predic-

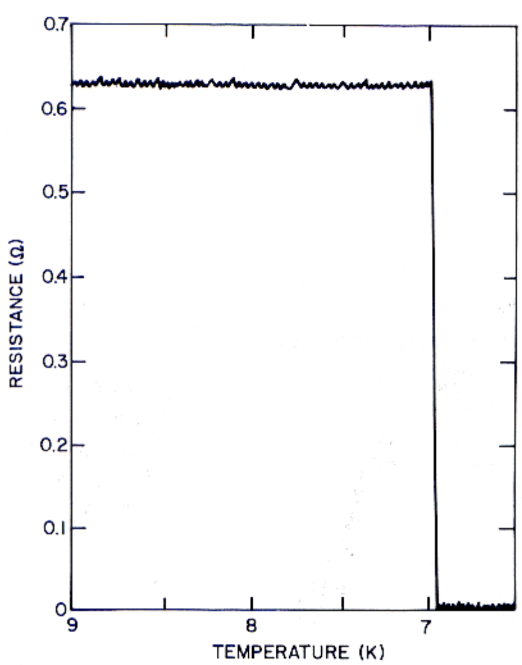


Fig. 13. Measured superconducting transition temperature for a Nb/Cu sample. Note the narrow width of the transitions.

ted by the Fuchs–Sondheimer theory [5]. At very small thicknesses the resistivity saturates at the minimum metallic conductivity value (so called Ioffe–Regel limit [6]). Similar behavior is observed for the Nb/Cu system. The

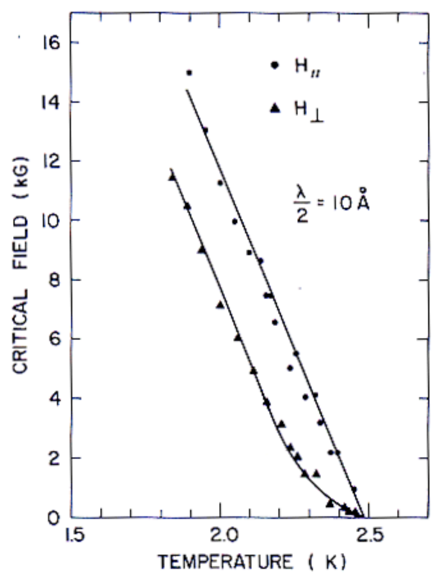


Fig. 14. Superconducting critical fields parallel and perpendicular to the layers for a Nb(10 Å)/Cu(10 Å) sample.

detailed temperature dependence for Nb/Cu samples shows a transition to a non-metallic like behavior for thin layers (resistivity decreasing with increasing temperature). This observation and its relation to dimensionality will be the subject of a future publication.

Nb is a superconductor with a transition temperature of 9.2 K and Cu is a normal metal. The superconducting transition temperatures measured inductively or resistively on these samples are in close agreement and are dependent upon layer thickness. Fig. 13 shows the resistance versus temperature for a Nb(52 Å)/Cu(52 Å) sample. The transition width (~ 60 mK) is quite narrow indicating the absence of large distribution of inhomogeneities. The superconducting critical fields are anisotropic (see fig. 14) indicating that the effective electronic masses are different perpendicular and parallel to the layers. We note that since the coherence length for the Nb/Cu superlattice is larger than the layer thickness, the theories appropriate for layers coupled by tunelling are not applicable here. The experimentally measured anisotropy is dependent on layer thickness and detailed experiments are underway to compare to theoretical predictions for highly anisotropic superconductors.

5. Summary

In summary, structural studies indicate that sputtering is useful for the preparation of metallic superlattices. The Nb/Cu system shows long range structural coherence (~ 10λ) perpendicular to the layers. The physical properties are also indicative of the layered nature of the material and detailed studies are underway to answer questions related to the effect of dimensionality of physical properties.

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