Magnetic and structural features of thin tantalum films with a fivefold symmetry axis

V. G. Trubachev, A. I. Tovstolytkin, and A. P. Shpak
Institute of Metal Physics, Ukrainian Academy of Sciences, 252142 Kiev, The Ukraine

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Structural and magnetic properties of thin films formed from an ensemble of tantalum clusters with a fivefold symmetry axis have been studied in fields up to 200 Oe. The magnetic response of pentagonal tantalum clusters is sharply higher than that of bulk tantalum. A shift of the hysteresis loop characteristic of complex noncollinear magnetic materials is observed at $T=5$ K after the films are cooled in an external magnetic field. It is suggested that the anomalies observed in the magnetic properties are due to the icosahedral symmetry of the clusters.

Metal clusters are interesting entities in the physics of the condensed state and have attracted research interest in recent years. The reason for this interest is not solely that these clusters occupy an intermediate position between isolated atoms and bulk solids. There is the further motivation that, when the clusters are formed under certain conditions, one experimentally observes the onset of fivefold symmetry axes, which are forbidden by the laws of classical crystallography. Such a cluster as an independent entity is of interest from the standpoint of its special physical properties, e.g., magnetic. There is the possibility that this one distinguishing feature may prove exceptionally significant in an ensemble of such clusters with dimensions of 1–10 nm.

In this letter we are reporting a study of the magnetic properties of an ensemble of tantalum clusters with a fivefold symmetry axis in the form of two films on thin (5-μm) mylar substrates. The thickness of the layer of pentagonal tantalum clusters formed on the substrate was either $\sim$100 nm (film 1) or $\leqslant$1000 nm (film 2). We observed a substantial difference between the magnetic properties of the tantalum pentagonal clusters and those of bulk tantalum with a bcc lattice.

The test samples with the deposited tantalum clusters were studied by x-ray diffraction and high-resolution transmission electron microscopy (JEM-2000 FXII). For the x-ray diffraction we used an HZG-4A universal diffractometer with Fe $K\alpha$ radiation. Measurements were taken out point by point over several passes. A characteristic feature of the fragment of the diffraction pattern shown in Fig. 1 is that it contains lines of the metastable modification of tantalum with the fcc lattice, which is not characteristic of the macroscopic state of tantalum. The high-resolution electron microscopy revealed the habit of the tantalum clusters, which is characteristic of a cluster with pentagonal symmetry. The onset of fivefold symmetry axes in clusters with sizes on the order of 10 nm can apparently be discussed at a qualitative level in this case as resulting from a collective behavior of an ensemble of identical fcc crystals in the shape of tetrahedra, many of which are twinned. Note the distinction between this symmetry type, inherent in pentago-

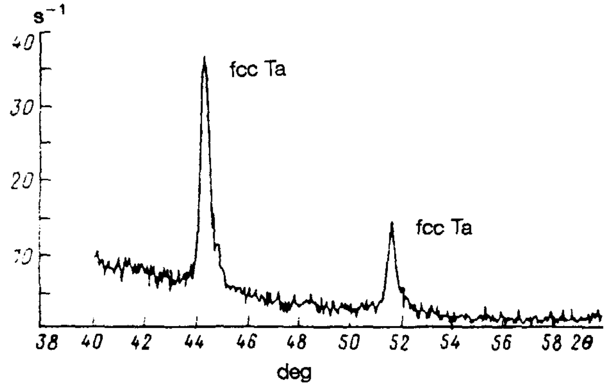

FIG. 1. Fragment of a diffraction pattern from pentagonal clusters of tantalum formed in a film ~100 nm thick (film 1).

nal clusters of pure tantalum, and the quasicrystalline symmetry characteristic of quasicrystals.[1]

The magnetic behavior of the films of the tantalum pentagonal clusters was studied with a SQUID magnetometer in fields up to 200 Oe. The results on the magnetic properties of the tantalum pentagonal clusters (film 1) are shown in Fig. 2. Magnetization curve 1 was found through a cyclic change in the magnetic field H after the sample was cooled from room temperature to $T=5$ K in the absence of an external magnetic field. The onset of a hysteresis on the plot of $M(H)$ was rather unexpected. As is known, tantalum, which has a bcc structure up to its melting point in the bulk state, is a $5d$ transition model, which does not have a magnetic order anywhere in the temperature range.[2,3] Our measurements of the magnetization of a tantalum sample with a volume two orders of magnitude greater than the volume of the tantalum pentagonal clusters (film 1)

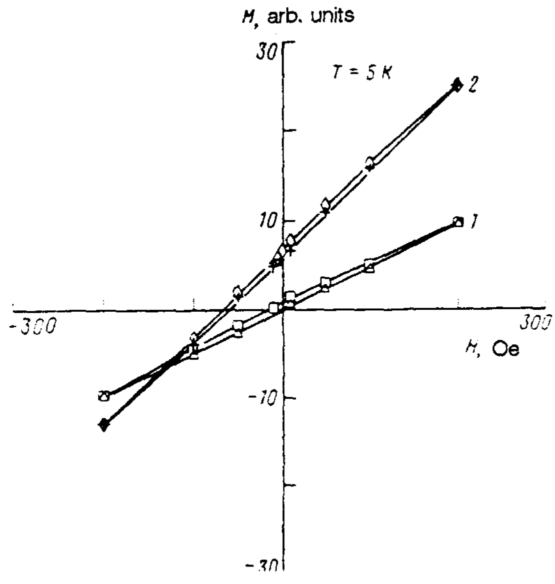

FIG. 2. Hysteresis loops at $T=5$ K after film 1 was cooled in a magnetic field $H_c=200$ Oe (curve 2) or without this field (curve 2).

failed to reveal a weak useful signal against the background of the signal from the sample holder. Consequently, the magnetic response of the tantalum pentagonal clusters is at least two orders of magnitude higher than that in bcc tantalum.

Hysteresis loop 2, found after cooling of film 1 from $T \sim 50$ K to 5 K in an external magnetic field $H_c = 200$ Oe, is extremely interesting. In comparison with curve 1, there is a significant increase in the remanent magnetization M_r, and there is an increase in the slope. The ratio of M_r to the magnetization in a field of 200 Oe, $M(200)$, is 0.28 for curve 2. The 60-Oe shift of the hysteresis loop in the direction opposite the magnetic field applied during the cooling is extremely interesting. In negative fields, at $|H| > 120$ Oe, the absolute values of the magnetization in state 2 are higher than in state 1. Such features are not characteristic of simple types of magnetic order; they may be viewed as an indication of the existence of a bulk anisotropy.[2,4] A set of properties like those of tantalum pentagonal clusters has been observed in several noncollinear magnetic materials with a unidirectional anisotropy,[2,5,6] but in the case of tantalum pentagonal clusters the nature of the onset of the complex magnetic order remains unclear.

The magnetic properties of film 2 are not qualitatively different from those of film 1. Expressed per unit volume, however, the magnetization is severalfold lower than in film 1, while the ratio $M_r/M(200)$ has increased to 0.5 (for the case of cooling in a magnetic field $H_c = 200$ Oe). The decrease in the specific magnetization of the sample may be due to an increase in the relative amount of crystalline bcc tantalum as a result of phase transitions upon an increase in the number of clusters in the ensemble.

The effect of an icosahedral symmetry on the properties of Al and Al–Mn alloys was studied theoretically in Ref. 7. The results of calculations on the electronic structure of Al clusters with icosahedral symmetry are quite different from corresponding calculations for clusters with cubic symmetry. For icosahedral clusters, the density of states at the Fermi level is anomalously high, and the electron binding energy is 0.8 eV higher.

In Ref. 8, we found the tantalum $4f$ spectrum of pentagonal clusters on an ÉS-2402 x-ray-photoelectron spectrometer. The main tantalum peaks in the spectrum, $4f_{7/2}$ and $4f_{5/2}$, are narrow and clearly defined, indicating an impurity-free homogeneous state of the tantalum atoms in the pentagonal clusters. The tantalum spectrum is shifted 1.4 eV toward higher binding energies in comparison with that of bcc tantalum. It is quite likely that the energy shift of the spectrum of pentagonal clusters observed experimentally and the sharp increase in the magnetic response of the tantalum pentagonal clusters in comparison with bcc tantalum are due to the icosahedral symmetry.

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