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A scientific session of the General Physics and Astronomy Division of the Russian Academy of Sciences was held in the P L Kapitza Institute of Physics Problems on 26 January 1994. Two papers were presented:

(1) **S M Klotsman** "Local structures, and diffusion, dynamic, and electronic properties of interface cores and adjoining regions of crystallites";

(2) V V Ustinov "Giant magnetoresistance effect in metallic superlattices."

An abridged version of the first paper is given below.

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Local structures, and diffusion, dynamic, and electronic properties of interface cores and adjoining regions of crystallites

S M Klotsman

The relative volume of the interface cores in the usual polycrystalline samples does not exceed 10^{-4} and the corresponding volume of the dislocation cores is 10^{-8} . In view of the correspondingly low densities of the specific states associated with the cores of these defects, information on the properties of the cores can be obtained only under exceptional circumstances. The specific states localised in the dislocation cores or at interfaces can be investigated by a method proposed by the present author [1], in which use is made of:

(i) *the atomic probes* capable of providing spectral information on the states which are filled by the atomic probes when they are introduced by diffusion into the investigated system; the Mossbauer nuclei used as the atomic probes provide such information;

(ii) the ionic superconductivity of the dislocation and interface cores for selective filling of the positions in the cores of such defects; the ionic superconductivity means that, at temperatures at which materials are normally used (not exceeding $0.2T_{\rm mp}$, where $T_{\rm mp}$ is the melting point), the diffusion coefficient in the dislocation and interface cores is ten orders of magnitude higher than the diffusion coefficient in the lattice.

The emission nuclear gamma resonances (NGR) or Mossbauer spectrum is measured after introduction of

Uspekhi Fizicheskikh Nauk **164** (4) 443–446 (1994) Translated by A Tybulewicz ⁵⁷Co atomic probes by annealing a polycrystalline sample. The ionic superconductivity state usually results in a complex population of the atomic-probe states in the core of a defect and in the adjoining parts of the lattice. The occupied atomic-probe states in the lattice of crystallites (grains) act as an internal standard [2] which can be used to calibrate the unknown properties of the defects. The method is universal because it is based on the common occurrence of the ionic superconductivity of the cores of structure defects.

Fig. 1 shows examples of the NGR (Mossbauer) spectra obtained for polycrystalline materials. An increase in the annealing temperature reduces the area under one line until it vanishes at high temperatures. This component of the Mossbauer spectra disappearing at high temperatures is due to the atomic probes localised in the interface cores of crystallites. Fig. 2 shows typical population curves of two types of states as a function of the reciprocal ξ of the of annealing temperature [3]. At high temperatures (near the intersection point ξ_{IP}) the populations of the states vary in full agreement with the phenomenological description of the ionic superconductivity in a polycrystalline sample. The possibility of determination of the relative concentration of the atomic probes (or of the populations of the states) in the interface cores and in the adjoining regions of the lattice has led to the development of a method for separate determination of the diffusion coefficients of these regions in a crystal and of the width of the interface core [4] (attempts to do this have been unsuccessful for several decades). As a consequence, a new mechanism of 'pumping out' of the atomic probes from the interface cores has been discovered: it is due to the appearance of vacancy-impurity complexes near the interface cores.

Table 1 gives the differences $\delta_{21} = \delta_2 - \delta_1 \pmod{s^{-1}}$ of the isomeric shifts of the states 2 and 1 in the intrinsic limit [5] of the investigated monatomic metals. In the majority of the materials in which the ⁵⁷Co atomic probes are small-radius impurities the difference δ_{21} is positive.

This general trend is due to the compression of the atomic probes in the interface cores. The positive difference between the isomeric shifts δ_{21} in such systems is due to an increase in the density of the intrinsic s electrons at the nuclei in the atomic probes. This state of the atomic probes may be reached under normal conditions only if the probes are at interstitial positions of the interfaces and the volume of these interstices is naturally less than the volume of an atomic probe. However, in the materials in which the ⁵⁷Co atomic probes are not small-radius impurities, for example in Cr and in n-Fe [6], the cobalt can no longer occupy the interstitial positions in the core of a defect. Then only because of the absence of volume changes the isomeric shift



Figure 1. Nuclear gamma resonance (Mossbauer) spectra of polycrystalline Pt after annealing at various temperatures, T_{ann} .

 δ_2 is governed by the density of the s conduction electrons in the interface core [7]. The density of the conduction electrons in the interface cores of 3d materials is thus less than in a regular lattice.

Two different positions, substitutional and interstitial, may be occupied in the structure of the interface cores of crystallites. However, the energy parameters of the ionic superconductivity of any atomic probes are practically indistinguishable within the structure-defect cores in a given



Figure 2. Occupancy of the states 1(1) and 2(2) filled by the atomic probes in palladium after annealing at various temperatures.

material. For example, in the case of tungsten the parameters of the ionic superconductivity of ¹⁸¹W and ⁵⁷Co are simply identical for the same homological temperatures [8, 9]. This means that the diffusion in a defect core represents collective motion which smooths out the individual features of the atomic probes employed.

The dynamical properties of the local environment of the atomic probes can be determined on the basis of the dependence of the probability of a nuclear gamma resonance (NGR) or of the area A_i of a component of the NGR (Mossbauer) spectrum on the measurement temperature T_{meas} . It is evident from Fig. 3 that the NGR probability increases as a result of cooling, as expected, but this happens in a limited range of T_{meas} . Below a certain value of T_{meas} the NGR probability falls in the case of palladium, platinum, rhodium, and iridium. Before discussing this 'anomaly' we shall consider the dynamical properties of the states labelled



Figure 3. Dependence of the area under the component 1 of the NGR spectrum on the measurement temperature.

Table	1.

v	Cr	n-Fe	Nb	Мо	Rh	Pd	Ta	W	Ir	Pt	Au
+0.2	-0.2	-0.1	+0.7	+0.7	+0.2	+0.1	+0.4	+0.5	+0.25	+0.10	+0.4

2, which are localised in the defect cores. The Debye temperature of these states is 1.5-2 times less than of the states labelled 1. This result can help in the understanding of the nature of the ionic superconductivity of the dislocation and interface cores.

Let us consider again the again the 'anomalous' behaviour of the NGR probabilities at low measurement temperatures. Fig. 4 shows an NGR spectrum obtained for Pt (the absorber velocity scale is compressed). At 5.5 K a characteristic sextet of lines is resolved: it indicates magnetic splitting of the nuclear levels of the atomic probes. The observed 'anomalous' fall of the NGR probability observed at low tempera-tures is therefore due to a magnetic phase transition in the regions of localisation of the atomic probes. The intensity is simply transferred from a narrow window used to ensure a high resolution of the NGR spectra (measured at 297 and 179 K) to the range of high absorber velocities, which is responsible for the anomaly of the dependences $\ln A_i(T)$. The temperatures of the onset of this magnetic transition are different for the defect cores and the bulk of crystallites (Fig. 5): these temperatures fall and approach one another as the purity of the material is increased. However, the magnetic transition does not disappear even in very pure Pd and Pt. These results are supported by recent theoretical [10] and experimental [11] investigations of the clusters of 4d transition metals. Obviously the magnetic phase transitions discovered by the present author in two-dimensional regions of the interface cores and the adjoining parts of crystallites are due to the same reasons as those occurring in the clusters of 4d



Figure 4. Nuclear gamma resonance spectra of Pt, plotted on different scales of the absorber velocity and recorded at different temperatures.



Figure 5. Dependences of the areas under the components 1(1) and 2(2) of the NGR spectra on the measurement temperature.

metals: a considerable narrowing of the d band and the appearance of sharp electron density peaks near the Fermi surface. It is evident from Fig. 3 that the temperature of the onset of the magnetic transitions in an interface core is half that in the parts of the lattice adjoining the core. The presence of a magnetically active impurity in a cluster [10] masks the change in the density of states due to a change in the cluster symmetry. Consequently, in our system containing such magnetically active impurities we can also employ the known [12] dependence of the magnetic transition temperature on the concentration of these impurities and on the density of the conduction electrons in exchangeenhanced magnetic materials: $T_c \propto C_{MAI} n^{1/3}$, where C_{MAI} is a concentration of the magnetically active impurity and n is the conduction electron density. This relationship and our result $T_2 < T_1$ implies that $n_2 < n_1$, i.e. the average density of the conduction electrons in the interface cores is less than in the array of regions where magnetic phase transitions have been observed. A similar conclusion follows from the sign of the differences δ_{21} for the 3d metals Cr and Fe in which the atomic probes occupy interstitial positions in the interface cores. Consequently, the observed low density of the conduction electrons in the cores of defects encountered in 3d, 4d, and 5d transition metals is a common property of the cores of these structure elements in monatomic metals.

We have considered so far the intrinsic properties of the interface cores and of the adjoining regions of the lattice. At low temperatures near the interfaces the interstitial impurities give rise to segregation of vacancy-impurity complexes. Substitutional impurities (including vacancies) influence relatively weakly the parameters of the NGR spectra [13]. Therefore, in the first approximation, the influence of the main component (which is the interstitial impurity) of the vacancy-impurity complexes is manifested in the NGR spectra. Since the interstitial impurities increase the lattice parameter, it follows that the substitutional atomic probes which reach the 'pumping out' zone containing vacancy-impurity complexes become localised at sites characterised by an increased atomic volume. This reduces the density of the intrinsic s electrons at the nuclei of the atomic probes and also reduces the isomeric shifts of ⁵⁷Co in the emission NGR spectra. It is evident from Fig. 6 that the isomeric shift δ_1 does indeed decrease from the intrinsic to the minimum steady-state value, which is



Figure 6. Dependences of the isomeric shifts of the component 1(1) and 2(2) on the temperature of annealing of Pt.

measured under conditions corresponding to a steady-sate composition of the aggregates in the form of vacancyimpurity complexes. The states labelled 2 differ qualitatively from the substitutional positions in the 'pumping out' zone, since they are interstitial positions in the structure of the interface cores. Therefore, their response to segregation of these complexes is different: the isomeric shift of the states labelled 2 increases with increase in the concentration of the complexes when the annealing temperature is lowered. This is due to the fact that in interstitial solid solutions a region appears around each interstitial impurity where the volume of the interstice is less than in the pure material. The smallradius atomic probes experience at such interstices a pressure which increases on reduction in the interstice volume and on increase in the concentration of the vacancy-impurity complexes. Therefore, the isomeric shifts of such modified states 2 increase as a result of cooling, falling from the intrinsic to the steady-state values, the latter being associated with saturation of the concentration of the complexes. Fig. 7 shows the Arrhenius dependences of the isomeric shifts of the components of the NGR spectra obtained for polycyrstalline Au. We can see that in the 'pumping out' zone in Au there are no aggregates in the form of vacancy-impurity complexes, but in the interface



Figure 7. Arrhenius dependences of the isomeric shifts of the components 1 (1) and 2 (2).

cores the situation is the same as in simple metals that readily dissolve interstitial impurities. The linear parts of the dependences in Fig. 7 can be used to find the binding energies of these complexes in the region of localisation of the corresponding state: in Pd, Pt, and Au this energy is equal to the binding energy of the components in the vacancy-impurity complexes.

Studies of materials of practical importance have made it possible to identify the origin of the unique properties of nanomaterials produced by the vapour-condensation technology [14]. It has been found that

(i) the structure and the properties of the interfaces in such materials are independent of the crystallite (grain) size:

(ii) the bulk properties of the crystallites in such nanocrystals are very sensitive to their fabrication technology;

(iii) the unique macroscopic properties of nanocrystalline materials represent simply a manifestation of the little-known properties of the cores of one-dimensional and two-dimensional defects whose volumes in these materials are comparable with the crystallite volume.

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