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X-ray *K*-line shifts in metallic europium and samarium in the 77–1000 K range

A. E. Sovestnov, A. S. Ryl'nikov, O. I. Sumbaev, and V. A. Shaburov

B. P. Konstantinov Institute for Nuclear Physics of the Academy of Sciences of the USSR, Leningrad

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The shifts in the x-ray *K* lines of metallic Eu and Sm have been measured in the following phase transition regions: the antiferromagnetic–paramagnetic transition, the structural transition αSm→hcp, and the transition involving λ-anomaly in the heat capacity. The size of the shifts permits one to conclude that none of these transitions is associated with a change of more than 0.07 electron/atom in the number of 4*f* electrons.

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Phase transitions accompanied by anomalies in thermodynamic, magnetic, and electrical properties are observed in metallic Eu at $T_1 = 86$ K and $T_2 = 756$ K,[1] and Sm at $T_1' = 106$ K, $T_2' = 696$ K, and $T_3' = 835$ K.[2] At the low temperatures (T_1 and T_1') these are antiferromagnetic–paramagnetic transitions; the transition at $T_3' = 835$ K in samarium has been attributed with the αSm → h.c.p. structural transition[2]; the nature of the transitions at T_2 and T_2', accompanied by λ-anomalies in the heat capacity, has not been hitherto established so unambiguously. It is thought that the latter may be due to a rearrangement of the electronic structure of the metals e.g., thermal excitation of 4*f* electrons into the conduction band.[2,3]

The nature of phase transitions in the rare-earth elements involving transfer of a 4*f*-electron to the conduction band can be very conveniently investigated by studying displacements in the x-ray *K* lines.1) We have previously used this method in studies of isomorphous transitions in metallic Ce and SmS[4,5]; it has also been used in investigating $Gd_xSm_{1-x}S$, $Nd_xSm_{1-x}S$, and $Nd_xSm_{1-x}Se$.[6] In the present work an experimental determination was made of the shifts in the K_{β_1} lines of metallic Eu and Sm as a function of the temperature of the samples. The measurements were carried out by the procedure described earlier[4]; in the case of the high-temperature experiments ($T > 300$ K) the samples, in the form of foils (20×20×0.2 mm, purity according to data from the manufacturing factory 99.9%), were placed in quartz ampoules filled with argon and provided with an external heater. The temperature of the sample was determined by the heater current which was calibrated from the melting points of Sn, Zn, and Eu. The relative error in determining the temperature of a sample did not exceed 4%. The absence of oxidation and of irreversible changes in the specimens resulting from the high-temperature experiments was confirmed by checks on the shifts in the x-ray lines after the samples had returned to room temperature.

Figure 1 shows the variation in the K_{β_1}-line shifts of Eu and Sm with temperature (the shifts were measured against identical samples at room temperature). The analogous variations in the heat capacities $C(T)$ of these metals obtained in other work[1,2,7] are reproduced in the upper part of the figure. Within the limits of measurement errors the K_{β_1}-line shifts of Eu and Sm were close to zero at all the temperatures investigated. Since the K_{β_1}-line shifts upon total removal of a 4*f*-electron from

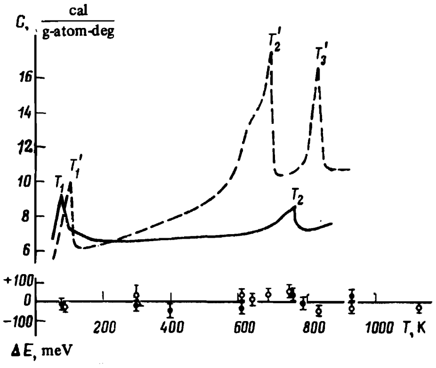

FIG. 1. Variation in the x-ray $K_{\beta 1}$-line shifts of Eu (full circles) and Sm (open circles) with temperature. The continuous and dotted lines show the behavior of the heat capacities of Eu and Sm[1,2,7] respectively.

the atoms of Eu and Sm are respectively equal to $\Delta E = -1450 \pm 40$ and -1455 ± 40 meV[8] it may be unambiguously concluded that none of the above phase transitions is accompanied by a change of more than $\eta \approx \pm 0.07$ electron/atom[2] in the number of $4f$ electrons in Eu and Sm.

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[1] In view of the anomalously deep position (in the radial direction) of the $4f$-electron in the atom its removal or excitation leads to significant changes (shifts) in the energy of the K lines.

[2] An analogous result was obtained by us in studying the ferromagnetic–paramagnetic transition in metallic gadolinium ($T_c = 290$ K).

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Superconducting transition temperature, critical magnetic fields, and the structure of vanadium films

A. A. Teplov, M. N. Mikheeva, V. M. Golyanov, and A. N. Gusev

I. V. Kurchatov Institute of Atomic Energy

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The superconducting transition temperature T_c, the perpendicular critical magnetic field $H_c^{\perp}$, the electrical resistance, and the structure of vanadium films obtained by ionic evaporation in an ultrahigh vacuum apparatus were investigated. A carbon sublayer and coating of 15 Å thickness were applied in order to protect the samples against external influences. The critical fields were measured by the resistive method. Upon a decrease of the film thickness from 2900 to 60 Å a reduction of T_c from 5.1–5.2 to 2.4 K was observed, along with an increase of the residual resistivity ρ_n from 4.5 to 20 μohm-cm and an increase of the derivative $|dH_c^{\perp}/dT|$ near T_c from 3.6 to 6.7 kOe/K. No superconductivity was observed in a film of 30 Å thickness down to 1.3 K. The type of crystal structure and the lattice constant for 125–1000 Å thick films, determined by the technique of electron diffraction, are the same as those for bulk samples of vanadium; the grain size in these films amounted to 500 to 800 Å. The electron density of states $N(0)$, calculated on the basis of the data concerning $|dH_c^{\perp}/dT|$ and ρ_n for thick films (720 to 2900 Å), agrees with the value of $N(0)$ for bulk vanadium (if it is assumed that the coefficient, which takes account of the correction due to strong coupling effects for H_{c2}, is given by $\eta = 1.2$). Upon a reduction of the film thickness to 60 Å, $N(0)$ is reduced by approximately a factor of two. The obtained results agree with the assumption that strong variations of $N(0)$, having an influence on T_c, can be observed in transition-metal films due to a reduction in the electron mean free path. The obtained quantitative information with regard to $N(0)$ in thin vanadium films ($d \leq 250$ Å) is sensitive, however, to the presence of a hypothetical surface transition layer and to its properties and thickness.

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1. INTRODUCTION

It follows from articles devoted to the investigation of the superconducting properties of vanadium films (a brief review of this problem is given in[1]) that:

1) These properties are very sensitive to impurities, and a transition temperature close to the T_c for pure, bulk vanadium (5.38 K) was obtained only for rather thick layers (thickness $d \gtrsim 2000$ Å) and for a rather small ratio of the fluxes of residual gas and metal on