

## Bunching of cerium valence in mixed-valence compounds

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Experiments reveal that cerium has a valence  $\approx 3.13$ ,  $\approx 3.27$ , or  $\approx 3.39$  in intermetallic compounds of mixed valence. The effect is explained on the basis that the different valence values correspond to different final states of a  $4f$  electron. It may be possible to use this bunching effect to identify the final state of the  $4f$  electron in a mixed-valence phase.

The phenomenon of mixed valence in compounds of rare-earth elements is one of the topics being studied most actively in solid state physics (see Ref. 1, for example). It is believed that the transition of a rare-earth atom from its “normal” integer valence state to a mixed-valence state, initiated by the composition, the pressure, the temperature, etc., is due to the excitation of an electron from an inner  $4f$  shell to outer  $6s(p)$  and  $5d$  levels of the conduction bands. The mixed-valence state is regarded as a resonance between two energetically close states of the rare-earth atom,  $4f^n$  and  $4f^{n-1} + e$ , which are determined by the initial and final states of the  $4f$  electron. The population of the  $4f$  shell (and its change) is therefore a fundamental characteristic of the mixed-valence state. A more complicated question is that of determining the specific final state of the electron  $e$ . To the best of our knowledge, there is no reliable experimental method at all for doing this.

The mixed-valence effect is seen most extensively in compounds of Ce and Yb. In



It can be seen from this histogram that the values of  $m$  cluster in a narrow interval  $3.1 \lesssim m \lesssim 3.4$  and in three tight groups (with six or seven materials in each group). The weighted-average values of  $\overline{\Delta n_{4f}}$  and the outer standard deviations for these groups are  $\overline{\Delta n_{4f}^{(1)}} = 0.13 \pm 0.01$ ,  $\overline{\Delta n_{4f}^{(2)}} = 0.27 \pm 0.01$  and  $\overline{\Delta n_{4f}^{(3)}} = 0.39 \pm 0.01$ , i.e., in its mixed-valence state, cerium "prefers" to have a valence value near  $\approx 3.13$ ,  $\approx 3.27$ , or  $\approx 3.39$ .

This bunching can be explained quite simply by treating the  $Ce^{3+}, 4f^1 - Ce^{4+}, e$  transition as an Anderson transition,<sup>6</sup> i.e., by assuming that the transitions (fluctuations) of a  $4f$  electron from site to site (from a cerium ion to a neighboring cerium ion) occur only between coincide (degenerate) energy levels. In this case the probability for finding a cerium ion in the  $4+$  state (this is the valence of cerium) it is determined exclusively by the multiplets  $M_{3+} = (2J_{3+} + 1)$  and  $M_{4+} = (2J_{4+} + 1)$  of the ground states of  $Ce^{3+}$  and  $Ce^{4+}$ :  $P(4+) \approx M_{4+} / (M_{4+} + M_{3+})$  [The high-lying excited terms contribute little to  $P(4+)$  at low temperatures.]

Let us consider some possible versions of the transition from the state  $Ce^{3+}, 4f^1, J_{3+} = 5/2$  to the state  $Ce^{4+} + e$ : 1) the transition  $Ce^{3+}, 4f^1 - Ce^{4+}, 6s_{1/2} ({}^6p_{1/2}), J_{4+} = 1/2$ ; 2) the transition  $Ce^{3+}, 4f^1 - Ce^{4+}, 6p_{3/2} (5d_{3/2}), J_{4+} = 3/2$ . For these versions we find  $P(4+) = 0.25$  and  $0.40$ , respectively.<sup>2)</sup> Finally, there is the possible version in which the  $4f$  electron does not localize at a neighboring cerium ion and instead goes into the valence band of the ligand: 3) the transition  $Ce^{3+}, 4f^1 - Ce^{4+}, J_{4+} = 0$ . This version corresponds to  $P(4+) = 0.14$ .

These calculated valences of cerium are shown by the dashed lines at the top of histogram *a* in Fig. 1; the filled circles show the rms experimental values with the external standard deviations. The experimental results agree well with the theoretical results. Accordingly, the valence of Ce takes on values near 3.14, 3.25, or 3.40, depending on where the  $4f$  electron goes during the formation of the mixed-valence phase.

Central histogram *b* in Fig. 1 shows the distribution of the Ce valence in the same compounds, but at a high temperature ( $T \approx 1000$  K). The high-temperature experiments may be thought of as a control experiment for the bunching effect. As the temperature is raised, the high-lying terms of the excited state of  $Ce^{4+}$  begin to be populated along with terms of the ground state. Furthermore, a temperature increase may also cause a deformation of the energy spectrum of  $Ce^{3+}$  and  $Ce^{4+}$ . This deformation should cause a mixing of the various versions of the  $4f \rightarrow e$  transition, i.e., should "smear" the groups, as is observed experimentally.

An analysis similar to that described above has been carried out for all the compounds of Yb which we studied which exhibit a mixed-valence state.<sup>7,8</sup> The results are shown by histogram *c* in Fig. 1. We see from this histogram that, again in the case of Yb, essentially all the values of  $m$  are clustered in the narrow interval  $2.75 \lesssim m \lesssim 2.9$ . The theoretical values of the valence of Yb for the various versions of the states  $Yb^{2+}, 4f^{14} - Yb^{3+}, 4f^{13} + e$  analogous to those discussed above yield values of 2.75, 2.83, 2.89, and 2.93 (these values are shown by the dashed lines on histogram *c*). These theoretical valences form a tight group which is "unresolvable" in this analysis. The rms valence of Yb in the region  $m \gtrsim 2.7$  is  $\bar{m} = 2.79 \pm 0.02$  (the filled circle on histogram *c*).

In summary, this bunching of the valences of Ce can be used to identify the final state of the  $4f$  electron during the formation of a mixed-valence state. This ability in turn makes it possible to draw general conclusions about the electronic structure of the rare-earth ion in this particular state.

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<sup>1</sup>The data obtained in Ref. 2 on  $Ce_{\alpha}$ , with a calibration based on  $CeO_2$ - $CeF_3$ , were converted for the  $CeF_4$ - $CeF_3$  calibration shift.

<sup>2</sup>Another possibility is a transition to a  $5d_{5/2}$  state. In this case we would have  $P(4+) = 0.5$ , but, as can be seen from histogram *a*, the group corresponding to  $m = 3.5$  is not observed. The apparent reason is that the multiplet  $5d_{5/2}$  lies significantly above the  $5d_{3/2}$  multiplet.

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<sup>2</sup>V. A. Shaburov, A. E. Sovestnov, and O. I. Sumbaev, *Phys. Lett.* **49A**, 83 (1971).

<sup>3</sup>V. A. Shaburov, A. E. Sovestnov, I. A. Markova, E. M. Savitskii, O. D. Chistyakov, and T. M. Shkatova, *Fiz. Tverd. Tela (Leningrad)* **23**, 2455 (1981) [*Sov. Phys. Solid State* **23**, 1437 (1981)]; **23**, 2827 (1981) [*Sov. Phys. Solid State* **23**, 1652 (1981)].

<sup>4</sup>Yu. P. Smirnov, A. E. Sovestnov, V. A. Shaburov, E. M. Savitskii, and T. M. Shkatova, in: *Tezisy dokladov III Vsesoyuznoi konferentsii po fizike i khimii redkozemel'nykh poluprovodnikov (Proceedings of the Third All-Union Conference on the Physics and Chemistry of Rare-Earth Semiconductors)* Tbilisi, 1983, pp. 32-36.

<sup>5</sup>O. I. Sumbaev, *Usp. Fiz. Nauk* **124**, 281 (1978) [*Sov. Phys. Usp.* **21**, 141 (1978)].

<sup>6</sup>P. W. Anderson, *Phys. Rev.* **109**, 1492 (1958).

<sup>7</sup>V. A. Shaburov, A. E. Sovestnov, E. M. Savitskii, I. A. Markova, O. D. Chistyakova, and T. M. Shkatova, *Fiz. Tverd. Tela (Leningrad)* **24**, 263 (1982) [*Sov. Phys. Solid State* **24**, 147 (1982)].

<sup>8</sup>M. N. Groshev, E. M. Levin, R. V. Lutsiv, N. M. Miftakhov, Yu. P. Smirnov, A. E. Sovestnov, A. V. Tyunis, and V. A. Shaburov, in: *Tezisy dokladov XIV Vsesoyuznogo soveshchaniya po rentgenovskoi i elektronnoi spektroskopii (Proceedings of the Fourteenth All-Union Conference on x-Ray and Electron Spectroscopy)*, Irkutsk, 1984, p. 88.

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