Title

FIRST MACROSCOPIC OBSERVATIONS OF THE CHEMICAL PROPERTIES OF BERKELIUM AND CALIFORNIUM (oral presentation - Geneva)

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Early this year microgram amounts of the elements berkelium and californium became available as a result of the irradiation of Pu^{239} with neutrons for a period of about 5 years. The production of these elements is described in a paper to be published in the proceedings of this conference. The present comments are added as a supplement.

Heretofore, the study of the chemical properties of berkelium and californium has been severely limited by confinement to the techniques of tracer methods. Thus it became important to attempt for the first time to investigate these elements by macroscopic observations. We have now been successful in measuring the magnetic susceptibilities of tripositive ions of berkelium and californium and it has been possible to set limits on the intensities of the absorption lines of these ions in the range of wave lengths from 4600 to 7500 Å.

ABSORPTION SPECTRA

The absorption spectra of the elements were studied by passing an intense light through a capillary cell with optically flat windows. Collimators were mounted at each end and defined a narrow beam of light (corresponding to the capillary dimensions (0.3 mm) that passed only through the solution. The transmitted light was then examined with a simple bench spectrometer with glass optics. The length of the capillary was about 10 cm and the cell volume was approximately 8 microliters.

Approximately 0.5 micrograms of berkelium and one microgram of californium dissolved in dilute hydrochloric acid were studied in this cell. Careful examination failed to reveal absorption by either berkelium or californium. Under the same conditions, the 5700 Å and 5200 Å absorption bands of about 2 micrograms of neodymium were readily visible. It is therefore concluded that neither Bk(III) nor Cf(III) aqueous ions are strongly colored and that the intensities of any absorption lines in the visible region must be such that their moler extension coefficients are much less than 20.

The failure to observe absorption lines of Bk(III) ions in the visible region of the spectrum is not surprising in view of its expected ground state

configuration of $^7F_6$. For Cf(III) however, Jørgensen has predicted absorption distributed over most of the visible region arising from transitions from the $^6H_{15/2}$ ground state to the various ^6F levels. Our results suggest that the transition probabilities are diminishing in the heavier as compared to the lighter actinides. Recent studies of the absorption spectrum of Cf(III) by a photographic method have revealed the presence of two broad weak absorptions, with the maxima at around 7800 and 8300 Å respectively. They are shown in Slide 1 along with absorption lines of Dy(III) in the same region of the spectrum. It is possible that the transitions responsible for the Cf(III) absorption correspond to transition between analogous energy states of Dy(III), as suggested by the connecting dotted lines.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

The magnetic susceptibilities of tripositive ions of berkelium and californium were measured after sorbing them on a single 0.5 mm diameter bead of Dowex-50 4% cross-linked resin in the hydrogen form. The apparatus used for the measurements is illustrated in Slide 2. The bead was transferred to a very small mylar plastic basket attached to a quartz fiber 30 cm in length and 12 microns in diameter. This assembly was suspended in a tube which was filled with helium gas. The tube was surrounded by a quartz dewar container into which liquids ranging from liquid nitrogen to hot water could be placed to vary the temperature at which measurements were made.

The entire assembly was placed in a fixed position between the poles of an electromagnet. The magnetic susceptibilities of berkelium and californium were compared with those of similar amounts of gadolinium at the same temperatures and field strengths, by measuring the deflection of the resin bead with a microscope. Suitable diamagnetic corrections for the basket, fiber and resin bead were made in a similar fashion. The deflections produced by 0.056 micrograms of californium and 0.201 micrograms of gadolinium at several temperatures and magnetic field settings are shown in Slide 3. Similar data were obtained in the comparison of 0.23 micrograms of berkelium with 0.264 micrograms of gadolinium.

The gadolinium was sorbed from a solution of known concentration containing tracer amounts of either Am^{241} or Cm^{244}. Distributions between the resin bead and solutions were determined using standard counting techniques and, assuming equal distribution coefficients for curium, americium, and gadolinium, the amount of gadolinium adsorbed could then be calculated. The direction of the errors introduced by the assumption of equal distribution

coefficients is such as to make the final magnetic susceptibility measurements of berkelium and californium slightly low.

From Slide 3 it can be seen that the deflections obtained at a constant magnetic field setting vary linearly with the reciprocal of the absolute temperature. The ratios of deflection for Gd(III) and Cf(III) at each temperature and field setting were used to calculate the magnetic susceptibility of californium. The same method was used for berkelium.

The measurements of gadolinium show good agreement with the Curie Law as expected. The data on Bk(III) and Cf(III) deviate appreciably from the Curie Law. The data are then fitted by a Curie-Weiss type of relation with small Δ values. The experimental errors, particularly at the higher temperature, are fairly large and may account in part for the deviation. However, crystal field interactions with the ground state multiplets could lead to the observed behavior, and may in fact be responsible for it. In any event the deviations are relatively small and effect the calculated values of the moments only slightly.

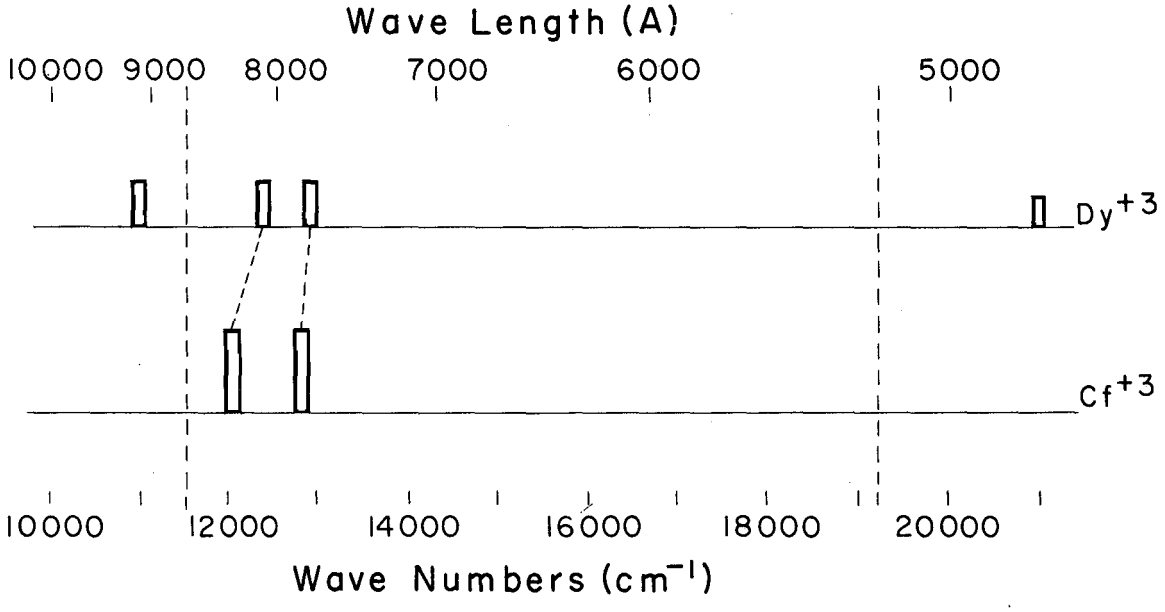
In Slide 4 are presented the effective magnetic moments of ions of the transuranium elements containing from 1 to 10 sub-shell electrons. The moments have been calculated directly from the experimental measurements of the susceptibilities (generally, from observations near room temperature). The points shown also include the values 8.7 and 9.2 Bohr magnetrons for berkelium and californium, respectively, calculated from the average of our experimental data taken at five temperatures and two field settings. The standard deviation in the susceptibility values relative to gadolinium was ±5%. As to the absolute values of the susceptibilities, we believe these cannot be in error by more than 20%, with a corresponding error in the derived moments of not more than 10%. The theoretical values for Bk(III) and Cf(III) are 9.7 and 10.6 respectively. We show for comparison on the same figure theoretical values of the magnetic moments for various numbers of sub-shell electrons calculated according to three different sets of assumptions: (a) the electrons occupy "f" orbitals and interact by pure L-S coupling, unperturbed by external fields of any kind. (b) The electrons are in "d" orbitals, with complete quenching of the orbital momentum and (c) the electrons occupy "f" orbitals with complete orbital quenching.

As is well known, the observed magnetic moments of the lanthanide element compounds are closely in accord with (a) above, and the moments of "d" transition series compounds agree rather well with (b).

The third possibility must be considered also, as it cannot be excluded a priori. The experimental data on the transuranium elements clearly agree best with the derived moments calculated from our first set of assumptions. The susceptibilities of Bk(III) and Cf(III) are much higher than predicted by the "spin only" formulae, and approach rather closely the values found experimentally for the rare earth ions containing the same number of subshell electrons. There would seem to be no further doubt that current evidence on the bulk magnetic properties of the transuranium elements strongly supports the actinide hypothesis.

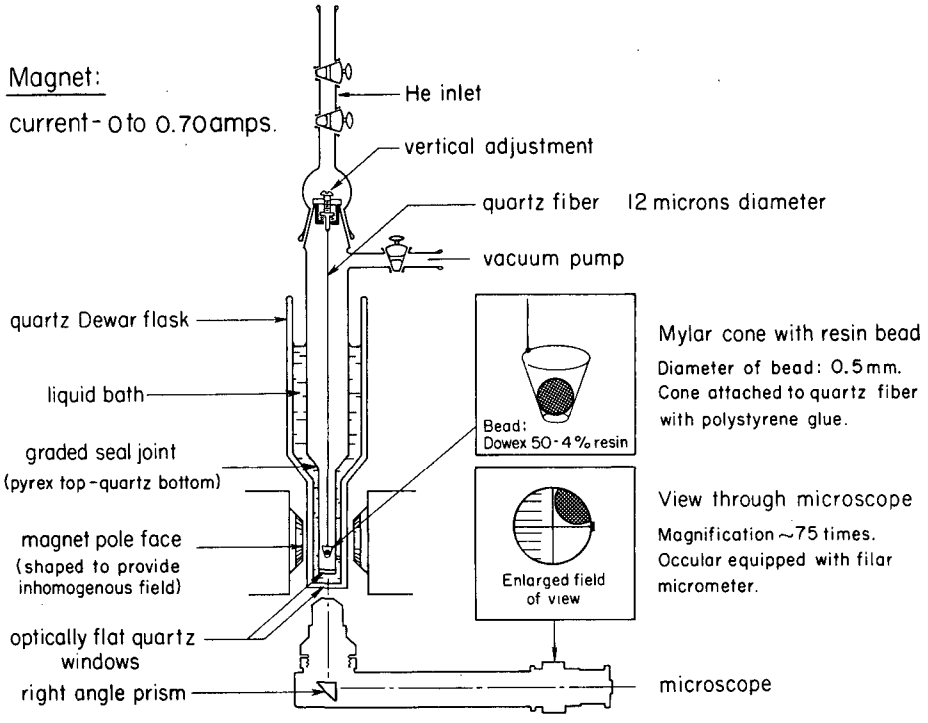
Solution absorption spectrum of Cf^{+3}

(The wavelength range inside the dotted lines was explored)



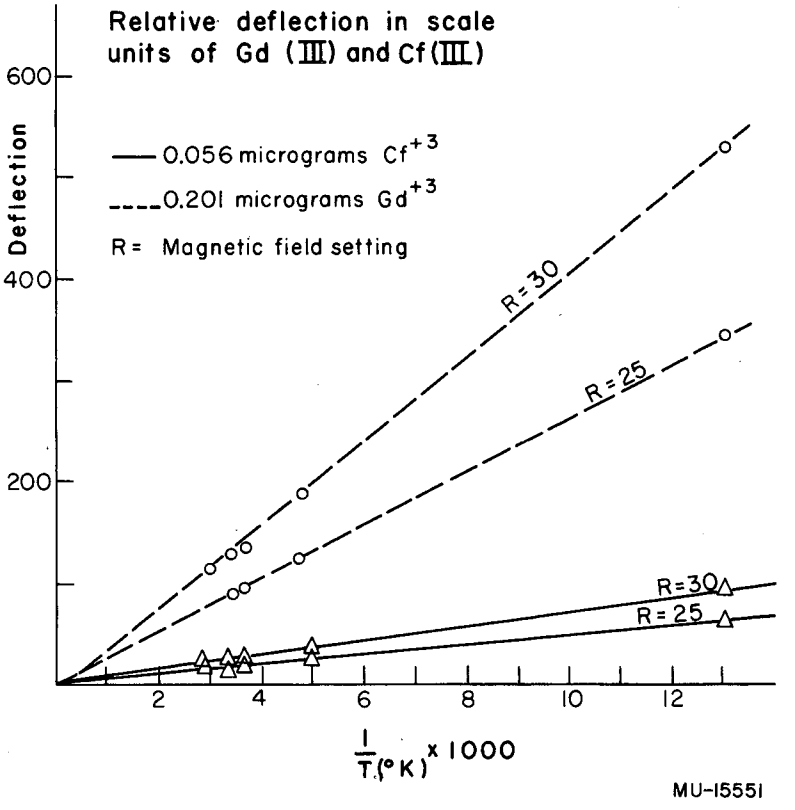
MU-15726

Slide 1

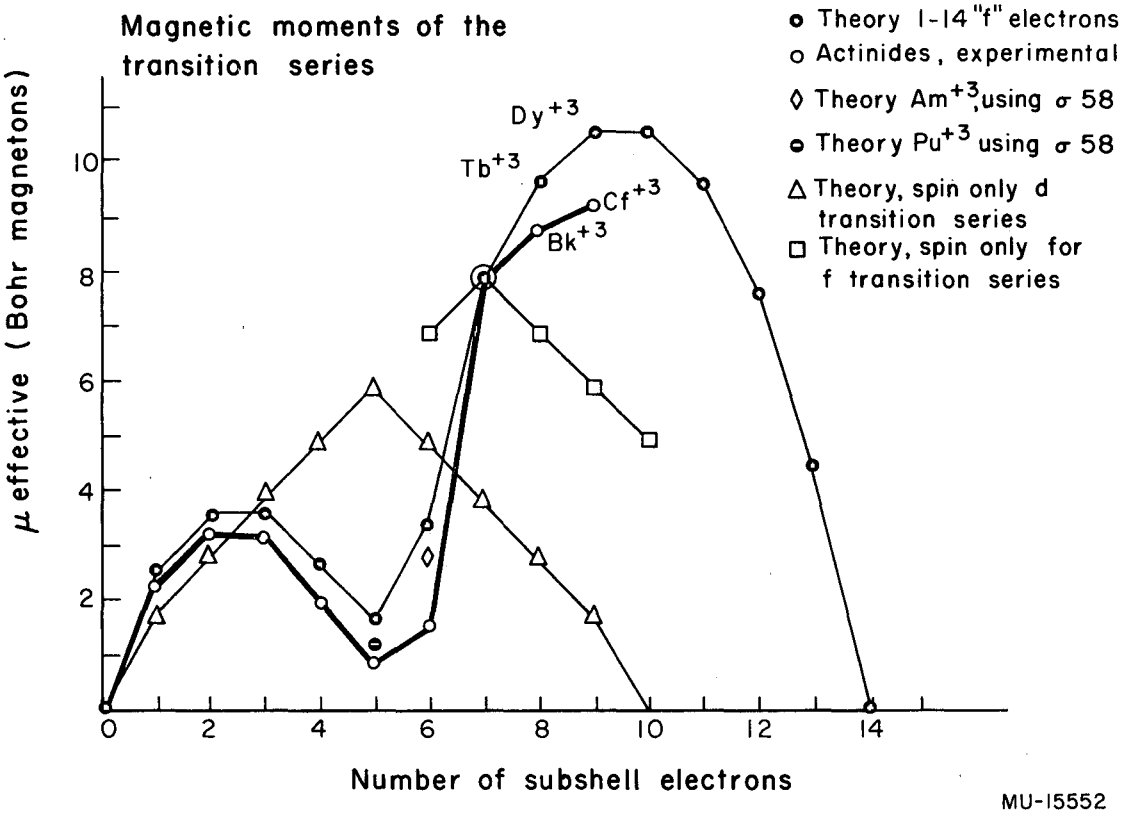


MUB-204

Slide 2


Relative deflection in scale units of Gd (III) and Cf(III)
600
400
200
Deflection
0.056 micrograms Cf^{+3}
0.201 micrograms Gd^{+3}
R = Magnetic field setting
R=30
R=25
R=30
R=25
2
4
6
8
10
12
$\frac{1}{T(°K)} \times 1000$
MU-15551

Slide 3


Magnetic moments of the transition series
μ effective (Bohr magnetons)
Number of subshell electrons
Dy+3
Tb+3
Cf+3
Bk+3
Theory 1-14 "f" electrons
Actinides, experimental
Theory Am+3 using σ 58
Theory Pu+3 using σ 58
Theory, spin only d transition series
Theory, spin only for f transition series
MU-15552

Slide 4