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EXPERIMENTAL EVIDENCE FOR THE SUPER COSTER-KRONIG DECAY

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3p-excitation of atomic Mn; experimental evidence for the super Coster-Kronig decay

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The experimental 3p-spectrum of atomic Mn is shown to be in good agreement with theoretical results based on the interference between the $3p^6 3d^5 4s^2 \rightarrow 3p^5 3d^6 4s^2$ and the $3p^6 3d^5 4s^2 \rightarrow 3p^6 3d^4 4s^2 \varepsilon f$ excitations mediated via the $3p^5 3d^6 4s^2 \rightarrow 3p^6 3d^4 4s^2 \varepsilon f$ super Coster-Kronig decay.

Stimulated by recent measurements of the 3p-absorption of Mn vapour and the detailed analysis of the spectrum reported by Connerade et al. [1] Davis and Feldkamp [2,3] have calculated the multiplet splitting and the oscillator strength of the Mn $3p^6 3d^5 4s^2\ {}^6S_{5/2} \rightarrow 3p^5 3d^6 4s^2$ (J = 3/2, 5/2, 7/2) transitions. The interference between these discrete excitations and the continuum transitions $3p^6 3d^5 4s^2 \rightarrow 3p^6 3d^4 4s^2 \varepsilon f$ has been taken into account by extending Fano's theory [4] to the case of many discrete states with many continua. [5] As has been pointed out by Connerade et al. [1] the above channels are strongly coupled by the super Coster-Kronig decay $3p^5 3d^6 4s^2 \rightarrow 3p^6 3d^4 4s^2 \varepsilon f$. Note that this super Coster-Kronig decay is indistinguishable from autoionization. The spectrum calculated by Davis and Feldkamp [2] and the experimental spectrum reported by Connerade et al. [1] are shown in Fig. 1. According to Davis and Feldkamp the $3p^6 3d^5 4s^2\ {}^6S_{5/2} \rightarrow 3p^5 3d^6 4s^2\ {}^6P_{3/2,\ 5/2,\ 7/2}$ transitions are broadened into the dominant, asymmetric absorption band. Due to decay selection rules [2] transitions to ${}^6D$ and ${}^6F$, responsible for the sharp lines at threshold are almost unaffected. The main features of the spectrum are reproduced by the calculations but there remains a series of marked discrepancies:

i the three weak ${}^6S_{5/2} \rightarrow {}^6F_{3/2,\ 5/2,\ 7/2}$ lines at the 3p-threshold predicted by the theory are missing in the experimental spectrum. Consequently Connerade et al. assigned the strong line at 47,80 eV to ${}^6S \rightarrow {}^6F$, whereas according to the theory it is mostly due to ${}^6S \rightarrow {}^6D$.

ii the two remaining sharp lines in the theoretical spectrum are due to transitions to ${}^4P$ final states which are strongly mixed with ${}^6P$ and ${}^6D$. In contrast to this Connerade et al. detected five structures in this energy range which they ascribed to ${}^6P$ and ${}^6D$ final states.

iii probably due to the overlap of higher spectral orders the spectrum of Connerade et al. does not show the pronounced Fano type profile of the dominant absorption band. Furthermore the marked shoulder is missing in the experimental curve and the broad band contains less oscillator strength relative to the sharp lines than calculated.

iiii the calculated energy separation between the sharp lines and the dominant maximum exceeds the separation determined experimentally.

To assess the validity of the theoretical approach we carefully reinvestigated the 3p-spectrum of atomic Mn.

The experimental set-up has been described previously [6,7]. The temperatures of the Mn vapour ranged from 1150°C to 1300°C, which corresponds to vapour pressures between 0.4 and 2.9 Torr. The atomic absorption lines of the buffer gases Kr and Xe [8] in first and second spectral order, superimposed on the absorption spectrum of atomic Mn served for the determination of the energy positions of the Mn absorption maxima listed in Table 1. We note that the values reported by Connerade et al. [1] are off by $\sim$ 0.3 eV. The assignment based on the calculations of Davis and Feldkamp [2] is included. The energy resolution at the 3p-threshold was 16 meV. The relative spectral dependence of the absorption coefficient has been established from a series of photopraphic plates obtained under different conditions (vapour pressure, exposure time, filters). For these exposures higher spectral orders have been suppressed by a carbon coated mirror (reflectivity < 4% above cut-off energy 130 eV) in front of the spectrograph, by Al-filters and by the buffer gas. Only the densitometer traces in wavelength regions covered by the plates for which the density of the plates was within the range of linear response were used. Spectra obtained under the same conditions were averaged. After correcting for the wavelength dependence of the spectrum without Mn, the spectra were normalized to one set of exposure time and Mn pressure. This was achieved by adjusting the relative heights of structures and the slope of the curves in regions wherethe spectra obtained under different conditions overlap. The spectrum of atomic Mn given in Fig. 1 has been normalized to the spectrum of metallic Mn [9] below and above the 3p-threshold.

Most of the discrepancies between theory and experiment discussed above are resolved by our measurements. The three weak lines (1 - 3) at the 3p-threshold predicted by Davis and Feldkamp clearly exist. In agreement with the theory a group of three, well resolved lines (4 - 6) follows towards higher energies. This confirms the statement by Davis and Feldkamp, that the splitting of the line at 48.8 eV (6) detected by Connerade et al.[1] is unreal.

The interaction with the continuum via the super Coster-Kronig decay manifests itself in the Fano type profile of the dominant absorption band. The maximum is split into two peaks. Identifying the low energy peak with the shoulder in the theoretical spectrum this is in accordance with the theory. The distribution of the oscillator strength determined experimentally is well reproduced by the calculations. Transitions to $3p^5 3d^5 4s^2 n\ell$ ($n > 3$) states or double excitations have not been incorporated in the calculations and therefore the lines above 54 eV are missing in the theoretical spectrum. Thus only two major discrepancies remain:

i the maxima (1 - 8) of the calculated spectrum span an energy range $\sim$ 2 eV wider than determined experimentally.

ii the calculations overestimate the width of the dominant absorption band.

Arguing that most of the correlation effects, which result in a reduction of the multiplet splitting, are contained in the interaction between the channels discussed above, Davis and Feldkamp did not scale the Slater parameters obtained by Hartree-Fock calculations [1]. The above discrepancies between theory and experiment can probably be remedied by scaling the Slater parameters, or by explicitly taking into account additional correlation effects which reduce the multiplet splitting and furthermore shift the higher excitations towards threshold.

In summarizing the above discussions we conclude that our data give further strong evidence for the interpretation of the 3p-spectrum of atomic Mn in terms of the model based on the super Coster-Kronig decay of the excited states. The similarity of the 3p-spectrum of metallic Mn, included in Fig. 1, and atomic Mn suggests, as has been pointed out before[3,1], that the same mechanisms determine the spectrum of the metal.

We are indebted to L.C. Davis and L.A. Feldkamp for making their results available to us, prior to publication.

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Table 1. Energy positions of the Mn 3p-absorption maxima. The numbers in brackets in column 2 give the relative uncertainty of the last digits. The absolute error of the experimental data is 0.02 eV The 21 structures detected in the energy range from 54.41 to 59.87 eV are omitted. The energies given by Davis and Feldkamp [2] and the assignment based on their calculations are included.

Peak	Energy (eV)		Assignment
	this work	theory [2]	
			Mn $3p^6 3d^5 4s^2\ {}^6S_{5/2}$ →
1	47.144 (9)	47.09	→ $3p^5 3d^6 4s^2\ {}^6F_{7/2}$
2	47.346 (11)	47.29	→ $^6F_{5/2}$
3	47.490 (20)	47.44	→ $^6F_{3/2}$
4	48.074 (-)	48.44	→ $^6D_{7/2,\ 5/2,\ 3/2}$
5	48.501 (4)	48.89	→ $^4P_{5/2}$
6	48.832 (9)	49.18	→ $^4P_{3/2}$
7	50.40 (5)	51.35	} $^6P_{7/2,\ 5/2,\ 3/2}$ +
8	50.83 (5)	52.13	} + $^4P,\ ^4D,\ ^4F,\ ^4G,\ ^4H$

Figure Caption

Fig. 1 3p-absorption of atomic (solid line) and metallic[9] (dotted line) Mn. The lower solid line gives the densitometer trace reported by Connerade et al.[1] The absolute absorption coefficient refers to the spectrum of metallic Mn. The oscillator strength df/dE for atomic Mn calculated by Davis and Feldkamp[2] is given by the dashed line.