Spin polarized photoemission studies of the 3s core levels in Fe and Co

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Abstract

Spin polarized photoemission is used to study the 3s core levels of Fe and Co. The exchange splitting between the two spin components in the main $3s3p^63d^n$ configuration is found to be larger in Co than Fe. The satellites corresponding to emission from the $3s^23p^43d^{n+1}$ configuration are identified in both metals. The application of a sum rule to obtain the spin moment from the complete spectrum including all configurations is investigated.

1. Introduction

The magnetic properties of surface and thin films have recently become the subject of intense research activity (see, for example, Ref. [1]). This increased interest reflects two important advances; firstly, the development of new techniques allowing the atomic engineering of technologically important materials [2] and secondly, the development of spin sensitive electron spectroscopies allowing the characterization of these new materials. In the latter area, spin sensitivity has been added to a number of spectroscopies that have previously been used in studies of the electronic structure and other properties of surfaces and thin films. Specific examples include spin polarized photoemission (see, for example, Ref. [3]) which has

been used to study the exchange split valence bands of ferromagnetic materials, and secondary electron microscopy with polarization analysis (SEMPA) [4] which has provided microscopic information on the magnetic structure of surfaces. However, the latter techniques are not site or element specific. Spectroscopies that are site specific include the spin polarized versions of Auger electron spectroscopy [5], core level photoelectron spectroscopy [6–11], magnetic circular dichroism (MCD) [12,13] and linear dichroism (LMD) [14]. These techniques rely on the excitation of a core level whose binding energy will be element specific and therefore, in principle, all are capable of providing information on local magnetic structure.

Core level photoemission from magnetic materials has been extensively studied in both spin-integrated and spin-resolved studies. The earliest studies of emission from the 3s core levels of such systems found evidence of a satellite that was not present in the spectra from non-magnetic materials [15,16].

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The satellite is generally interpreted as evidence of an exchange interaction between the final-state core hole and the net spin S in the valence bands. In a simple model due to Van Vleck the splitting ΔE between the satellite and main peak will reflect the net spin in the valence bands S such that

$$\Delta E = \frac{2S + 1}{2l + 1} G^l(3s, 3d) \tag{1}$$

where $G^l(3s,3d)$ represents the appropriate Slater exchange integral between the 3s and 3d level. However, several experimental studies indicate that the splitting is much smaller than would be expected on the basis of such a model [16] and configuration interaction of different multiplets in the final state has been invoked as a mechanism for explaining the observed reduction [17]. Such a mechanism requires the observation of satellites at a higher binding energy as has indeed been observed in studies of 3s core level photoemission from Mn, both in ionic compounds and in the gas phase [18].

Excitation from the 3p core level has been studied in both core level photoemission [6,7,11] and linear dichroism [14]. Unlike the 3s level, studies of the 3p level are complicated by the presence of the spin–orbit interaction, which for this level in the 3d transition metals, has a magnitude comparable to that of the exchange interaction. Indeed in experimental configurations where the spin orientation or magnetization of the sample is orthogonal to the plane of the incident light polarization, the spin–orbit interaction results in strong dichroic effects which modify the intensities of the different spin components in photoemission spectra [14,19]. A general observation of 3p core level studies is that the emission of minority spin electrons is more dominant than the emission of majority spin electrons and further that the "exchange" splitting between the main majority and minority spin components is considerably smaller than would be expected on the basis of the appropriate Slater exchange integrals. These characteristics have again been analyzed in terms of configuration interactions [20]. The imbalance in intensities of the two spin components has also been discussed in terms of a spin dependent filtering effect whereby minority spin electrons are more likely to emerge from the crystal [19].

There have also been a number of studies of the 2p core levels [11,13,21]. Indeed absorption at the 2p edge has proved to be one of the most studied effects in soft X-ray MCD [13]. For the 2p levels in the 3d transition series, the spin–orbit interactions are much stronger than the exchange effects and the interaction with the valence bands will be closer to the limit of j–j rather than LS coupling.

The total magnetic moment at a particular site may be divided into two contributions, the spin moment and the orbital moment. One question facing any new core level technique is whether or not it can provide information on these two properties. As an example, it is well established that MCD provides information on the orbital moment but it remains unclear as to how easy it is to obtain information on the spin moment from the same technique [22]. In this paper we review our own spin polarized photoemission studies of the 3s core level in ferromagnetic systems and examine whether it is possible to obtain information on the spin moment from such a technique.

2. Experimental

The experimental studies discussed in this paper were all carried out on the soft X-ray X1B beamline at the National Synchrotron Light Source [23]. This beamline based on a soft X-ray undulator produces a high flux of photons in the range 200–600 eV. The introduction of undulators in storage rings has proved extremely useful in low sensitivity techniques such as spin polarized photoemission [3]. In the present case, measurement of the energy and spin of the photoelectrons is accomplished using a hemispherical analyzer backed by a low energy spin detector [24] of the type developed by the NIST group [25]. The analyzer collects electrons over a solid angle of ±5°, which, for the present purposes, is effectively angle integrating. The angle of incidence of the light was approximately 60° and the angle of electron collection was 15° away from the surface normal.

Cobalt and iron films were grown using e-beam evaporation on Cu(001) and Ag(001) substrates respectively. For spin polarized photoemission

studies the films, which were of the order of 20 layers thick were magnetized in plane with an adjacent coil. However it should be noted that the spin detector was mounted to allow for detection of spins with the sample magnetized both in and out of plane [24].

3. Results and discussion

In Figs. 1 and 2 we show the spin integrated and spin resolved spectra obtained from the Fe(001) and Co(001) surfaces, respectively. The Fe spectra, which have been published previously [26] are reproduced here for completeness. The ratio of the intensity in the main 3s peak to the intensity in the background is typically 3 : 2. In the spin resolved spectra the total number of counts accumulated within the main 3s peak is typically 10^6.

For both Fe and Co we are clearly able to resolve two peaks in the majority spin channel corresponding to the high spin final state and the low spin final

state at higher binding energy. These states correspond respectively to total spin $S + \frac{1}{2}$ and total spin $S - \frac{1}{2}$ states where S represents the net spin of the electrons in the valence bands in the initial state.

In order to analyze in more detail the spectra shown in Figs. 1 and 2 we have fitted the individual spin components with Doniach–Sunjic line shapes. This procedure described in more detail elsewhere [26] involves fitting both a peak and a background to each individual component in the spectra. This is illustrated in Fig. 3 for the majority spin states observed for Fe. In Figs. 4 and 5 we show the fits but now with the peak and background added for each component in the Fe and Co 3s levels, respectively.

With appropriate values for the Slater exchange integrals [27] it would be expected on the basis of Eq. (1) that the splitting between the high spin and low spin states for Co would be slightly smaller (by a factor of 0.87) than that observed for Fe. However, our fitting indicates that the exchange splitting observed in Co (4.5 eV) is actually larger than the 3.5 eV splitting observed in Fe.
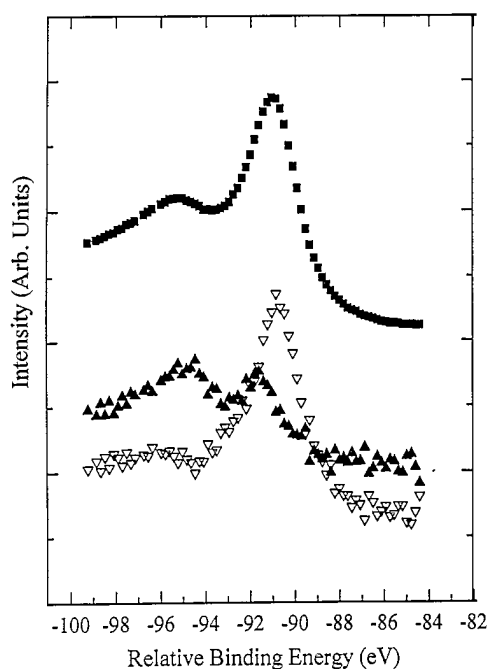

Fig. 1. Spin integrated and spin resolved photoemission spectra from Fe. The incident photon energy is 250 eV. The spin resolved spectra in the bottom half are indicated by the solid triangles for majority spin and empty triangles for minority spin.
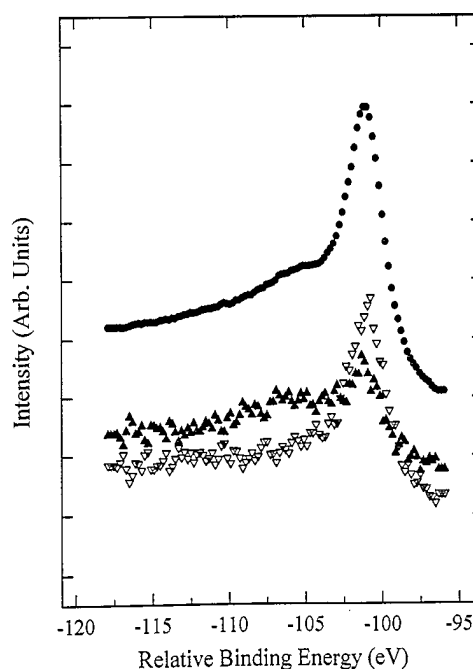

Fig. 2. Spin integrated and spin resolved photoemission spectra from Co. The incident photon energy is 250 eV. The spin resolved spectra in the bottom half are indicated by the solid triangles for majority spin and empty triangles for minority spin.
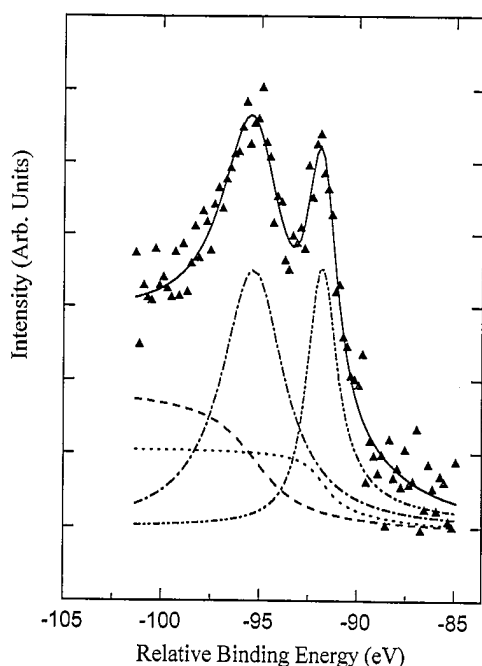
Fig. 3. The Doniach–Sunjic lineshape fits to the majority spin spectrum for Fe. The dot-dashed lines indicate the peaks. The long and short dashed lines indicate the backgrounds used for low and high spin states respectively.
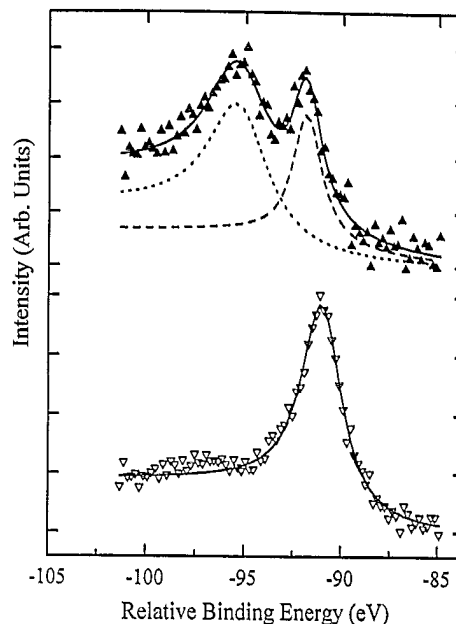

Fig. 4. The peak plus background fitted to each component in the spin spectra recorded from Fe. The majority spin spectrum is in the upper half of the panel. The minority spin spectrum is in the lower half.

Before discussing the relative intensities of the different peaks we first examine the line shapes or peak widths. For both Fe and Co the low spin final state is broader by a factor of approximately three than the high spin final states. Interestingly, this observation applies even to the majority spin component of the high spin state. Further, as we have previously noted elsewhere, the minority spin peak is broader than the majority spin peak in the high spin state. These individual peak widths, tabulated in Table 1, reflect the Auger decay life times of the

Table 1
Full widths at half maximum of the different spin components in the low and high spin final states as given by the Doniach–Sunjic line shape fits

	Low spin	High spin	
	Majority	Majority	Minority
Fe	1.86	0.75	1.19
Co	3.92	1.29	1.47

core holes. From the table it is clear that these life times are not determined simply by the spin of the core hole, as has been suggested frequently in the past, but rather by the LS configuration of the final state of the ion.

We now consider the intensities. The high spin state $S + \frac{1}{2}$ may have z components S_z equal to $S + \frac{1}{2}$ or $S - \frac{1}{2}$. The wavefunction, Ψ_{HS}, for this state is given by

$$\Psi_{HS} = A \left| S + \frac{1}{2}, \frac{1}{2} \right\rangle \left| S + \frac{1}{2}, -\frac{1}{2} \right\rangle$$

$$+ B \left| S + \frac{1}{2}, \frac{1}{2} \right\rangle \left| S - \frac{1}{2}, +\frac{1}{2} \right\rangle \quad (2)$$

Eq. (2) recognizes that to conserve S we must emit a photoelectron with spin $+\frac{1}{2}$ if the ion final state corresponds to $S - \frac{1}{2}$ and vice versa. Analysis of the Clebsch Gordon coefficient yields [28]

$$A = \sqrt{\frac{2S + 1}{2S + 2}} \quad \text{and} \quad B = \sqrt{\frac{1}{2S + 2}} \quad (3)$$
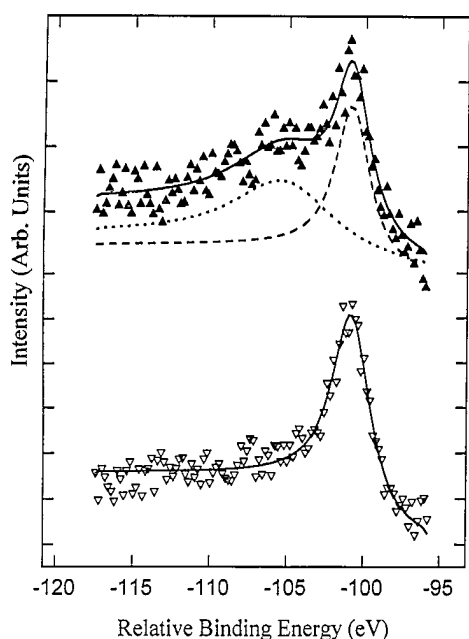
Fig. 5. The peak plus background fitted to each component in the spin spectra recorded from Co. The majority spin spectrum is in the upper half of the panel. The minority spin spectrum is in the lower half.

resulting in a spin polarization, P given by [29–31]

$$P = \frac{B^2 - A^2}{B^2 + A^2} = -\frac{S}{S+1} \tag{4}$$

The low spin state has only one z component $S = S - \frac{1}{2}$ with wavefunction Ψ_{LS} given by

$$\Psi_{LS} = C \left| S - \frac{1}{2}, \frac{1}{2} \right| S - \frac{1}{2}, +\frac{1}{2} \right\rangle \tag{5}$$

Here the photoelectron carries spin $+\frac{1}{2}$ resulting in 100% spin polarization for the higher binding energy peak in the spectrum.

We may compare the intensities predicted by such a model with the experimental observations. Calculations suggest that even in the presence of configuration interaction only the low spin state will lose intensity to the satellites [20]. The high spin state will retain its intensity. The model yields a ratio for the two components in this state, minority spin to majority spin, of $(2S + 1) : 1$. If we equate the magnetic moment with the value of $2S$ the predicted ratios for Fe and Co would be 3.2 and 2.6 respectively. Experimentally the observed ratios for

Fe and Co are 3.4 and 2.8, suggesting that this ratio will provide a reasonable measure of the spin moment. However, the intensities obtained by fitting the spectra in Figs. 1 and 2 depend heavily on the form of background that is used. Further, the ratio for Fe represents a ratio obtained from two peaks that are separated in binding energy by 0.9 eV [26]. The origin of this splitting, which has also been observed in a separate study of Fe [32], is not fully understood at the present time, although it may reflect the role of s–p electrons in the screening of the final state. We note from Fig. 5 that the splitting is also present in the spin resolved spectra of Co which show a separation of 0.2 eV in the binding energy of the two high spin components.

The relative intensities in the low and high spin states reflect the isotropic intensities. Thus in the single configuration the ratio of the two peaks in the majority spin channel will be $S : (S + 1)/(2S + 2)$ which reduces to $2S : 1$. Comparison with experiment shows that the experimental ratios are slightly reduced from this ratio, consistent with the presence of configuration interaction.

One important observation is that, unlike the case of 3p emission, a large percentage of the emission is present in the 3s spectra of Figs. 1 and 2. This raises the question of whether or not it is possible to use a sum rule to derive information on the local spin moment from the spectra. In a series of papers Thole and van der Laan have examined this question [19,33,34]. They consider the first moment of the spin spectrum $\int EI(E)dE$ where $I(E)$ is the intensity in the spin spectrum. The latter spectrum represents the difference between the two spin spectra of, for instance, Fig. 1. It may be calculated directly by taking the product of the isotropic intensity I_0 and the measured spin polarization P.

Thole and van der Laan [34] show that the first moment of the spin spectrum normalized to the isotropic intensity will be given by

$$\int EI(E)dE = \frac{-S}{2l+1} G^l(3s, 3d) \tag{6}$$

where as before $G^l(3s,3d)$ represents the appropriate exchange integral. From Eq. (6) we see that the first moment scales with the net spin in the valence bands.
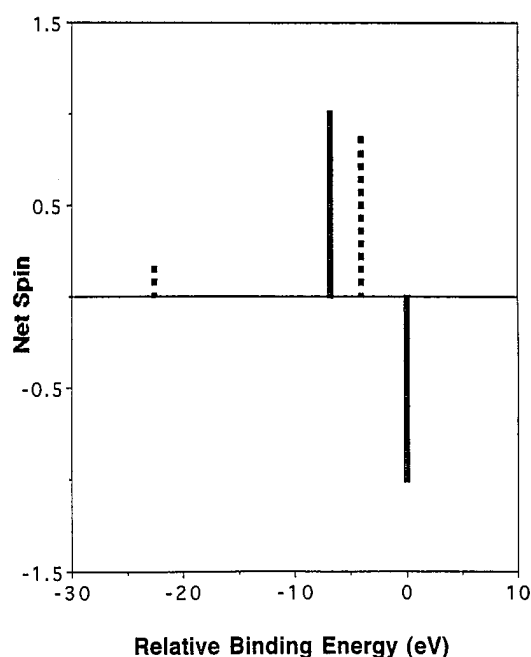
Fig. 6. Model calculation showing the application of the sum rule or first moment in the spin spectrum. The solid lines indicate that two components in the absence of configuration interaction. The dashed lines indicate the binding energies including the interaction with the satellite at higher binding energy. The net spin is normalized to the total spin in the valence bands. The upper half of the panel represents majority spin electrons, the lower half represents minority spin.

Let us consider the simple model of a low and high spin state separated in energy according to Eq. (1). If we take the atomic value of the exchange integral for Fe [27] we would calculate a splitting between the two states of the order of 6.8 eV. However, experimentally we find an exchange splitting of the order of 4.0 eV and a 15% reduction in the anticipated intensity of the low spin peak reflecting the presence of configuration interactions. We may apply the sum rule of Thole and van der Laan to examine where the intensity lost from the low spin peak has emerged in the spectra. This is demonstrated in Fig. 6. Initially we have two peaks in the spin spectrum separated in energy according to Eq. (1). From the multiplet analysis of Eqs. (2) and (5) we know that these peaks have equal intensity but opposite sign as indicated in Fig. 6 by the solid lines. If the sum rule of Eq. 6 is applied, it is a simple matter to show that the intensity lost from the low spin state must be transferred to a satellite

of majority spin character at the higher binding energy of 22.6 eV with respect to the high spin state. The shift of intensity from the low spin state is balanced by the reduction in the splitting between the low and high spin states observed experimentally. This "configuration interaction" is indicated by the dashed lines in Fig. 6. The high spin peak in the lower panel is unchanged by the interaction.

In the simple analysis above we have considered only a single satellite. It is possible that the intensity transferred from the low spin state is distributed between two or more satellites as suggested in a recent study of the role of configuration interaction in the Fe3s emission by Bagus and Mallow [20]. However our analysis suggests that if we measure the intensity and binding energies of the satellites together with the components in the main 3s emission, it should be possible to obtain a measure of the spin moment via the sum rule of Thole and van der Laan.

In Fig. 7 we show spectra recorded from Fe and Co films going through the region where the
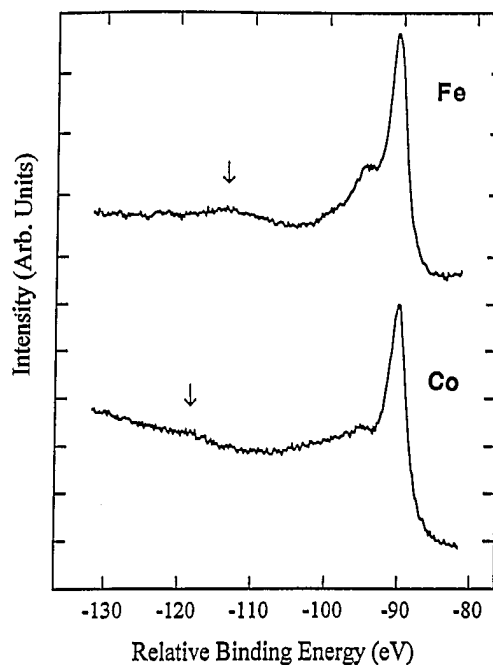

Fig. 7. Spin integrated spectra from Fe and Co showing the satellites indicated by arrows at higher binding energy. The incidence photon energy is 250 eV. The binding energy scale corresponds to the Fe spectrum. The Co spectrum has been shifted accordingly.

satellites are predicted to exist. Although relatively small, the satellites are clearly visible at binding energies of 22.0 eV and 29.0 eV for the Fe and Co, respectively. These measured binding energies are close to the values predicted in two separate calculations (21.9 eV for Fe [20] and 26.9 eV for Co [35]). Interestingly the intensity in the Co satellite is less than that observed in the Fe satellite. This is consistent with the observation that in Co the loss of intensity from the low spin peak (approximately 8%) and the reduction of the exchange splitting is less than that observed in Fe. The satellites shown in Fig. 7 represent emission from the $3s^2 3p^4 3d^{n+1}$ configuration. It would therefore be expected that the satellite will move to higher binding energies as one moves across the 3d transition row. This is illustrated in Fig. 8 where we plot the experimentally observed binding energies for Cr through Ni. The Cr and Ni observations will be published elsewhere [36]. The Mn result is taken from a study of ionic compounds and gaseous Mn [18]. It is interesting that the binding energy observed in the latter study falls below the line

joining the metallic observations in the present study. The difference probably reflects the relative screening.

4. Summary

The spin polarized photoemission studies of the 3s core levels discussed in this paper provide strong support for a model in which configuration interactions determine the relative splitting between the low and high spin states. This observation suggests that it is incorrect to take the measured splitting as a measure of the spin moment as has been found experimentally [37]. However our analysis of the first moment sum rule of Thole and van der Laan supports the idea that if it is extended over all configurations, it may well prove an effective way of obtaining site specific spin moment information from the photoemission spectra.
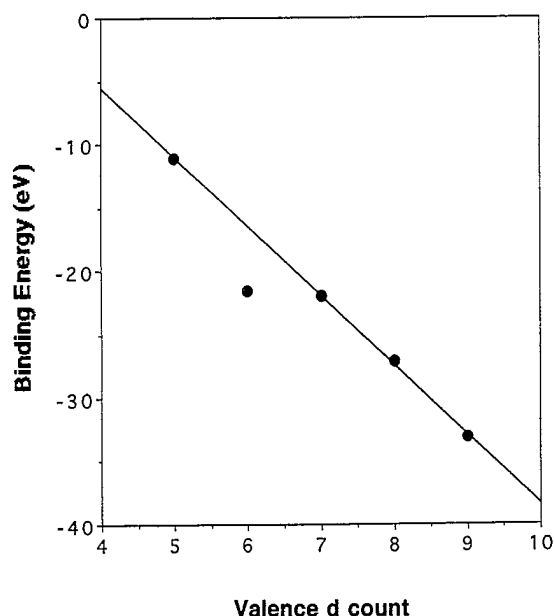
Fig. 8. Binding energies of the $3s^2 3p^4 3d^{n+1}$ configuration observed for Cr through Ni. The d count represents the d count applicable to the metallic state. The result for Mn (d = 6) is taken from Ref. [18]. The line is the best fit through the metallic measurements.

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