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Observation of dynamical spin-dependent electron interactions and screening In magnetic transitions via core-level multiplet-energy separations

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Abstract

The ferromagnetic-to-paramagnetic phase transitions for Gd(0001) grown on W(110) -a bulk transition at 293K and a surface transition about 85K above this- are found to influence the energy separation of the Gd 5s and 4s core-photoelectron doublets. The 5s doublet separation ΔE_{45s} changes over a range of temperatures spanning these transitions, and decreases by a maximum of 60 meV in this region, but then recovers its original value; the 4s doublet shows a smaller change in the reverse direction, which does not recover at high temperature. Some of these effects are semi-quantitatively understood from free-atom multiplet theory and from theoretical calculations based on all-electron LDA+U calculations including 4f electron correlation effects. However, the high-temperature behavior of the data also suggest a dynamical nature to these effects via spin-dependent electron screening that is influenced by magnetic fluctuations.

The multiplet splittings of core levels in transition metals and rare earths, as observed in photoelectron spectra, have long been a very useful probe of magnetism, providing sensitivity to both the valence electronic configuration and the local magnetic moment[1]. However, it has always been recognized that final-state relaxation and

screening effects need to be considered in interpreting such spectra[1,2]. With spin resolution of the outgoing photoelectrons and/or excitation by circularly polarized radiation[3], additional information on magnetic properties can be obtained[4,5]. The simplest multiplets arise from *s* core levels, which are dominated by a doublet of low-spin and high-spin final-states, are also inherently spin polarized, leading to a technique for studying short-range magnetic order as a function of temperature that has been termed spin-polarized photoelectron diffraction (SPPD)[4,6]. In a prior SPPD study of epitaxial Gd(0001) grown on W(110)[6], the intensity ratios of the 4s and 5s doublets (both of ^{7}S and ^{9}S character) showed strong variations with temperature near both the bulk Curie temperature T_{cb} of 293K and a higher surface-associated transition temperature T_s of 375K. Such effects have also been observed in several prior studies using other experimental methods[7,8,9,10,11,12], with the difference between surface and bulk transition temperature and interpretation varying from experiment to experiment, perhaps due to different surface preparation techniques and/or different degrees of surface or bulk sensitivity in the measurements. The possible influence of surface strain on the enhancement of a surface transition temperature for Gd/W has also been discussed[12,13]. Finally, a theoretical explanation of the enhanced surface transition temperature in terms of interlayer surface structural relaxation has also been proposed[14]. Noteworthy here is that core-level photoemission in general, or SPPD in particular, measures short-range magnetic order[4,6], thus perhaps being more sensitive to subtle near-neighbor and near-surface effects than some other measurements involving only long-range order.

However, our aim here is not to try to settle the issues surrounding the Gd(0001) surface and the different techniques and interpretations that have been applied to its magnetic transitions, but to demonstrate an additional type of short-range-order magnetic sensitivity in core-level multiplet splittings that is revealed via a careful measurements of the energy separation ΔE between the ^{7}S and ^{9}S states in *s* core-level photoemission, and show that such measurements should be a useful new probe of magnetic transitions, particularly in a time-resolved fashion as is now becoming possible via pump-probe experiments with high-harmonic generation lasers or free-electron lasers. In support of our conclusions, theoretical calculations at the free-atom and band structure level via a Koopmans' Theorem approximation confirm the interpretation of our data and agree semi-quantitatively with our measurements for the 5s spectra of Gd. Beyond this, a dynamical spin-dependent screening effect is suggested from the data. As a related example of what such future core-level measurements might reveal, we note a recent pump-probe photoemission experiment on Gd(0001) in which a rapid femtosecond scale drop was seen in the exchange splitting of a valence-band Δ_2 state, but with the minority band reacting much more rapidly than the majority band[15].

The measurements were carried out on bend-magnet beamline 9.3.2[16] at the Advanced Light Source in Berkeley, utilizing a photoelectron spectrometer/diffractometer with a Scienta ES-200 energy analyzer and a two-axis variable-temperature sample goniometer[17]. The Gd(0001) samples (the same used in the SPPD study[6]) consisted of bulk-like epitaxial films 100 ML or ≈ 300 Å thick grown on a W(110) single crystal substrate oriented to within 0.5° of (110). Gadolinium deposition was at

room temperature in an ambient pressure of 1-2 x 10^{-10} Torr. The films were then annealed to 725-750 K for 5 min., resulting in clean, well-ordered and atomically-smooth surfaces, as verified by both sharp hexagonal (1x1) LEED patterns and a separate study using scanning tunneling microscopy[18]. Core-level x-ray photoelectron spectra also verified that the surfaces were free of C and O contamination, and surface-sensitive valence-band spectra also showed an intense, sharp peak near the Fermi edge arising from the Gd(0001) surface state[11,12,19] before and after each experimental cycle. The temperature was increased from a minimum of 250 K (below T_{cb}) to 542 K, in steps of 6 to 10 K, with both Gd 4s and Gd 5s spectra being acquired at each step. Runs were also performed by decreasing the temperature downward from 542 to 250 K to ensure that all effects observed were reversible and in fact without hysteresis. The experimental geometry is shown in Fig. 1(a), and is the same as that reported previously[6]; the polar takeoff angle θ is defined with respect to the surface, and the $[10\bar{1}0]$ or "b" axis lying in the surface points along $\varphi=0^{\circ}$. Thus, the $[2\bar{1}\bar{1}0]$ or "a" axis points along $\varphi=90^{\circ}$. An angle of 70° was maintained between the linearly polarized light and the photoelectron analyzer entrance.

Typical photoelectron spectra from the Gd 4s and 5s regions have been presented previously (Figs. 1(b) and 1(c) in ref. 6), but we here show in more detail several for 5s emission in another direction as measured at three temperatures between 250 K and 430K. Each spectrum consists of a doublet containing the $ns^1...4f^7$ ^7S and ^9S final states possible when emitting a 5s or 4s core electron from the $...4s^2...4f^7 5s^2$ ... ^8S ground state of Gd into a dipole-allowed p photoelectron state. Photoelectrons emitted from the high-spin ^9S state are always at higher kinetic energy (lower binding energy) due to the energy-lowering effect of ns-4f exchange. From a standard derivation[4,6(b)], the ^7S photoelectrons can be shown to be 100% spin-polarized parallel with respect to the emitter spin, and the ^9S photoelectrons to be 77.8% spin-polarized anti-parallel. In describing the overall doublet splitting, the ns interaction with the three electrons in the free-atom configuration $[5d6s6p]^3$ that somehow occupy valence band states in the metal can to first order be neglected due to their highly delocalized nature and thus much reduced interaction strength with the more localized 4s or 5s orbitals, a neglect that has been confirmed in Gd 4d MCD studies [5,20]. However, because the 5s electrons share the same principal quantum no. (and thus approximate mean radial distribution) as the valence 5d electrons, they might be expected to be influenced to a greater extent by the more de-localized valence-band states, as we will see in more detail later.

Fig. 1(b) shows to some degree the effect of temperature on the relative intensities (cf. ref. 6) and also on the separation of the ^7S and ^9S peaks for the Gd 5s multiplet. The ^9S peaks have here all been normalized to be of equal height so that the small changes of 3 −5% in relative intensity can be directly seen via the ^7S peaks. Changes in the energy separation ΔE_{5s} are not easily visible directly from the spectra but were derived by fitting the doublets with two asymmetric Voigt functions of fixed but unequal widths riding on a Shirley-type inelastic background[6]. As the 5s and 4s multiplet peaks are well

resolved from one another at separations of 3.92 eV and 8.18 eV respectively, the intensity ratios and energy separations derived from them proved to be insensitive to the specifics of the fitting procedure utilized. In particular, we first fit the data with both peak widths and the separation between them free to vary. Then, with the peak width of each component fixed at the average over the full temperature range, the full set was again fit to yield intensity ratios or the closely related *spin asymmetry A* in SPPD defined elsewhere[6]. In particular, if the multiplet intensity ratio for 5s or 4s is $R(\theta,\phi,T) = (I_{7/2}/I_{9/2})(\theta,\phi,T)$, then the asymmetry is given by $A(\theta,\phi,T) = [(R(\theta,\phi,T) - R(\theta,\phi,T_{max}))/(R(\theta,\phi,T_{max}) + 2)]$ where $R(\theta,\phi,T_{max})$ is the measured peak ratio at the high temperature limit of the experiment (T = 542 K), which is assumed to be a point at which all long-range and short-range magnetic order has disappeared. Beyond this, fixing the separation at the average over all fits gave essentially identical intensity ratios, thus further verifying that changes in peak separation were not linked to the intensity ratio changes. The two sets of intensity ratios and separations agreed within experimental error of one another, and permitted resolving SPPD effects in both 5s and 4s spectra associated with the two magnetic transitions of Gd(0001)[6].

However, not discussed previously is the temperature dependence of ΔE_{ns}, which is compared to the temperature dependence of the intensity asymmetry for two different directions of 5s emission and one of 4s emission in Fig. 2. The ΔE_{4s} curves for both directions of 5s emission shown in Figs. 2(a) and 2(b) show broad minima with depths of about 60-65 meV that are nearly centered on the points of the two magnetic transitions at 293K and 375K. The ΔE_{4s} curve in Fig. 2(c) by contrast shows a monotonic increase with temperature and a less pronounced increase in ΔE_k by 40-50 meV over the range 280-380 K. Comparing these ΔE_{ns} curves with their corresponding intensity asymmetries in Figs. 2(a)-(c) is also revealing, in that the asymmetry in 5s for one direction (Fig. 2(a)) is sensitive to the magnetic transitions, but for the other direction (Fig. 2(b)) is not; the fact that both ΔE_{5s} curves show very similar minima further confirms the independence of the ΔE_{ns} results from the intensity asymmetry results. Making the same comparison for two sets of 4s results (the second is not shown here) also leads to the conclusions that the ΔE_{4s} and asymmetry results as we have derived them are both fully reliable. We further conclude that the 4s photoelectrons are more directly sensitive to the magnetic environment in their final-state scattering and diffraction via the asymmetry, while less sensitive than 5s as regards ΔE_{ns}, which also varies in the opposite direction.

In order to understand the changes in energy splitting more quantitatively, we begin by considering the simplest theoretical picture in terms of the Van Vleck Theorem of atomic spectroscopy[1,2]. In this model, the multiplet splitting arises due to the exchange interactions between the 5s (or 4s) and 4f orbitals, as embodied in the exchange integrals $K_{5s,4f}$ (or $K_{4s,4f}$). The energy separation of the high-spin and low-spin states is then given by:

$$\Delta E_{ns} = (2S + 1)K_{ns,4f} \qquad (1)$$

where S is the initial state spin (7/2 for Gd if we consider only 4f electrons) and $K_{ns,4f}$ is the exchange integral between the ns and 4f orbitals. If we utilize the tabulated Hartree-

Fock calculations of Mann[21] for $K_{5s,4f}$, a value of 3.62 eV is predicted for ΔE_{5s}. This is in excellent agreement with the experimentally determined 5s splitting range of (3.84 to 3.92 eV), as expected from prior work and the fact that correlation (configuration interaction) effects in the final ionic state are relatively small due to the limited overlap in space of 5s and 4f orbitals[2]. The 4s splittings are, on the other hand, not in this good agreement with simple theory, with present experiment at 8.18 eV and Van Vleck at 13.92 eV, such that experiment is only 58% of simple theory; this discrepancy for intrashell splittings has been discussed in detail previously, and is known to be due to greater correlation effects[2,22].

Thus, the general features of theoverall splitting values ΔE_{ns} are well understood, but what about the reproducible decrease of about 60-65 meV in 5s in going through the two magnetic transitions, and the smaller and opposite effects in 4s? We first note that about 0.63 μB of the Gd atom's 7.63 μB moment resides in the $(5d6s6p)^3$ valence electrons[14,23]. Therefore, a small component of the overall exchange splitting in the 5s spectrum should come from these valence electrons, but with an enhanced importance for 5s due to the higher degree of spatial overlap between 5s and 5d. Utilizing the aforementioned Hartree-Fock calculations[21] as a source for the additional exchange integrals $K_{5s,5d}$ and $K_{5s,6s}$, we can make a rough estimate as to the valence electron contribution to ΔE_{ns} by modifying the Van Vleck theorem to include valence overlap:

$$\Delta E_{5s}[5s, (5d6s)^3] = (2S_{VB} + 1)[f(5d)K_{5s,5d} + f(6s)K_{5s,6s}] \quad (2)$$

where we neglect the 6p contribution since free-atom exchange integrals are not available for it, f(5d) and f(6s) are the fractional occupations of the valence electrons in these shells and S_{VB} is the spin associated with the valence band (≈ 0.63/2). From the calculations of Wu et al.[23], we estimate f(5d) to be 25.3% and f(6s) to be 74.7%. This gives $\Delta E_{5s}[5s, (5d6s)^3]$= 0.60eV, or roughly 16.5% of the total splitting observed for 5s, compared to the actual change in ΔE_{5s} of 0.06 eV, which is about 10x smaller. Thus, small changes in these valence contributions to exchange that are also known to control ferromagnetic coupling in Gd via the RKKY interaction are also induced by passage through a magnetic transition might be expected to give rise to a decrease in ΔE_{5s} near both T_{cb} and T_s. Carrying out the same sort of calculation for 4s in this simple atomic picture shows that the valence-4s coupling is approximately 5x weaker, thus helping to explain why a reduced, and even inverse, effect is seen in Fig. 2(c).

A more accurate estimate of these effects has also been made based on band-structure calculations for Gd(0001)[14] based on the full-potential linearized augmented plane-wave approach together with the Hubbard U ("LDA+U")[24] to allow for correlation effects in the 4f electrons. These all-electron LDA+U calculations yield spin-resolved 5s and 4s core-level eigenvalues that can be used approximately via Koopmans' Theorem to estimate the binding energies and thus the multiplet splittings in both the ferromagnetic (FM) and anti-ferromagnetic (AFM) states of Gd. These are the two limiting "reference" states that would be fluctuating between one another as one passes through the magnetic transitions. The Fermi-level-referenced 5s binding energies are very well (in fact surprisingly well) predicted, with the two binding energies in experiment at 43.2 eV and 47.1 eV, and those in theory at 42.7 eV and 45.8 eV, respectively. The

multiplet splittings for the FM state are found to be 3.14 eV for 5s (somewhat smaller than free-atom theory at 3.62 eV and experiment at 3.88 eV, but still about 80% of the experimental value), and 5.89 eV for 4s (about 72% of experiment at 8.18 eV). Thus, we can expect these results also to give us some indication of the change in ΔE_{ns} on going from complete order into the FM-to-PM transition region (at which antiferromagnetic alignment first becomes possible on a larger scale), by taking a difference of the FM and AFM eigenvalues. This yields finally $\delta[\Delta E_{5s}(5s,\text{FM-AFM})] = 33$ meV, in semi-quantitative agreement with the 60-65 meV dip seen in ΔE_{5s}(expt.). Furthermore, $\delta[\Delta E_{4s}(4s,\text{FM-AFM})] = 10$ meV only, or less than 1/3 as large, with the further expectation that intrashell 4s-4f correlation effects[1,2,22] might act to further reduce the sensitivity to the transition, thus making it even smaller or reversing its sign, as suggested in experiment.

Although the above atomic and energy-band calculations, both based inherently on ground-state models, appear to qualitatively (or for 5s even semi-quantitatively) explain the magnitudes and systematics of the effects observed in ΔE_k, the fact that the 5s splitting returns to its FM value well above the transition temperature, and that both 5s and 4s show larger effects through the transition region, is more difficult to explain. Taking all of these effects into account suggests more generally a dynamical spin-dependent final-state screening of the 5s or 4s hole left behind that is slightly accentuated as the temperature passes through a point where there are large fluctuations in the adjacent valence electrons and the relative directions of the dominant 4f magnetic moments. That is, if near the transition regions (bulk or surface), the spin fluctuations and concomitant changes in screening ability involved affect a minority hole (that leading to ^{9}S) differently from a majority hole (leading to ^{7}S), then the separation between the two peaks could be changed. One way of viewing the interaction of the spin-polarized hole with its surroundings would be via the RKKY interaction [25], which could, through the oscillations in spin polarization induced around the hole, be very sensitive to the nature of the magnetic order or to fluctuations on the near-neighbor sites. A more quantitative estimate of this effect is beyond the scope of this paper, but as one final comment, the return of the 5s splitting to its FM value well above the transitions would follow from the spin-dependent screening argument above, since the fluctuations are expected to die out well above the transition temperature.

In conclusion, core photoelectron spectra show that the ^{7}S to ^{9}S peak separation of the Gd 5s multiplet in epitaxial Gd(0001) grown on W(110) varies systematically with temperature, showing a broad minimum with a 60-65 meV decrease as the temperature passes through both Tcb and Ts for this material, and finally returns to the FM splitting above these transitions. The analogous Gd 4s multiplet shows a smaller, and reverse, effect. The direction and approximate magnitudes of the effects in Gd 5s are also well predicted by relativistic LDA+U calculations and Koopmans' theorem, but with additional effects due to spin-dependent core-hole screening and near-transition fluctuations also being suggested to explain the behavior of both Gd 5s and 4s on going to higher temperatures. Although further experimental and theoretical study will be necessary to understand such effects fully, the measurement of such core-level splittings as a function of temperature, or in time-resolved pump-probe experiments on the femtosecond scale that are now becoming possible with high-harmonic generation

lasers or free-electron lasers, is promising as an element-specific probe of the electron dynamics in magnetic phase transitions.

As another relevant system in this regard, a temperature-dependent study of the manganite $La_{0.7}Sr_{0.3}MnO_3$(LSMO), has shown a much larger change of 1.1 eV in the corresponding Mn 3s multiplet splitting as temperature goes about 150K above the T_C of about 370K[26]. This has been attributed to an effective change of the Mn 3d occupation number by about unity via polaron formation. Although a much different system in that the 4f occupation number is unchanged in Gd on going through the transition, whereas the strongly correlated LSMO is inherently of mixed 3d occupation, studying such strongly correlated systems with very careful measurement of multiplet splittings on passing the magnetic transition, again perhaps in a pump-probe fashion to yield time resolution is a very interesting prospect[27].

As a final comment, since excitation of spin-orbit split core levels in photoemission with circularly polarized radiation is also known to produce j = ℓ+1/2 and j = ℓ-1/2 photoelectron peaks that are strongly and oppositely spin polarized[3], the binding energy separation of these two components could also be affected by the effects discussed here. Since the magnitude of the resulting photoemission magnetic circular dichroism (MCD) depends critically on the separation between the peaks involved as excited with the two polarizations[20,28], it is possible that the MCD could be appreciably enhanced during a magnetic transition, again suggesting an interesting avenue for study in a dynamical pump-probe fashion.

Figures:

Figure 1: (a) The experimental geometry, with emission angles θ and φ defined. (b) Experimental Gd 4s spectra as a function of temperature, for three temperatures spanning the two transitions at T_{cb} and T_s seen. (c) A blowup of the peak region in (b), to illustrate the subtle changes in the spectra with temperature.

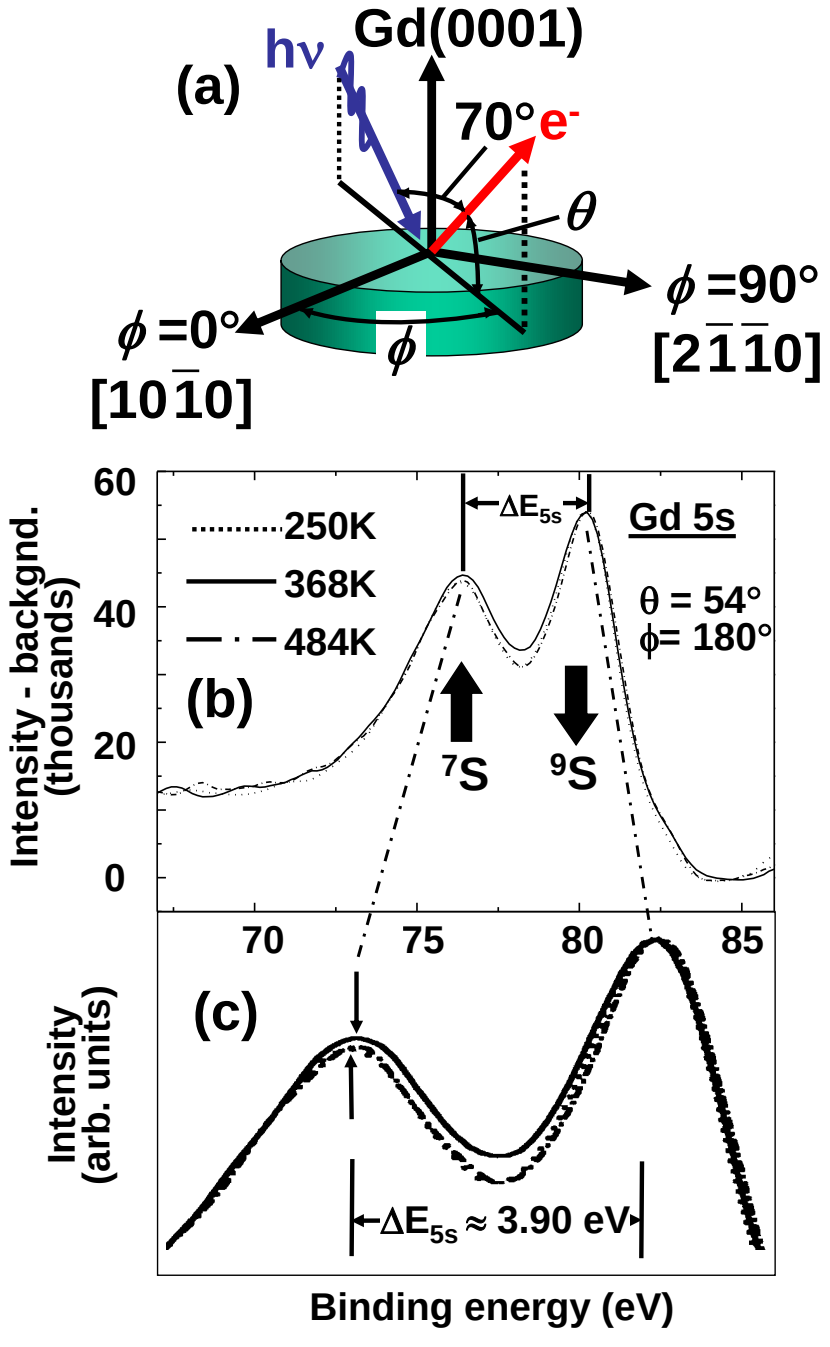
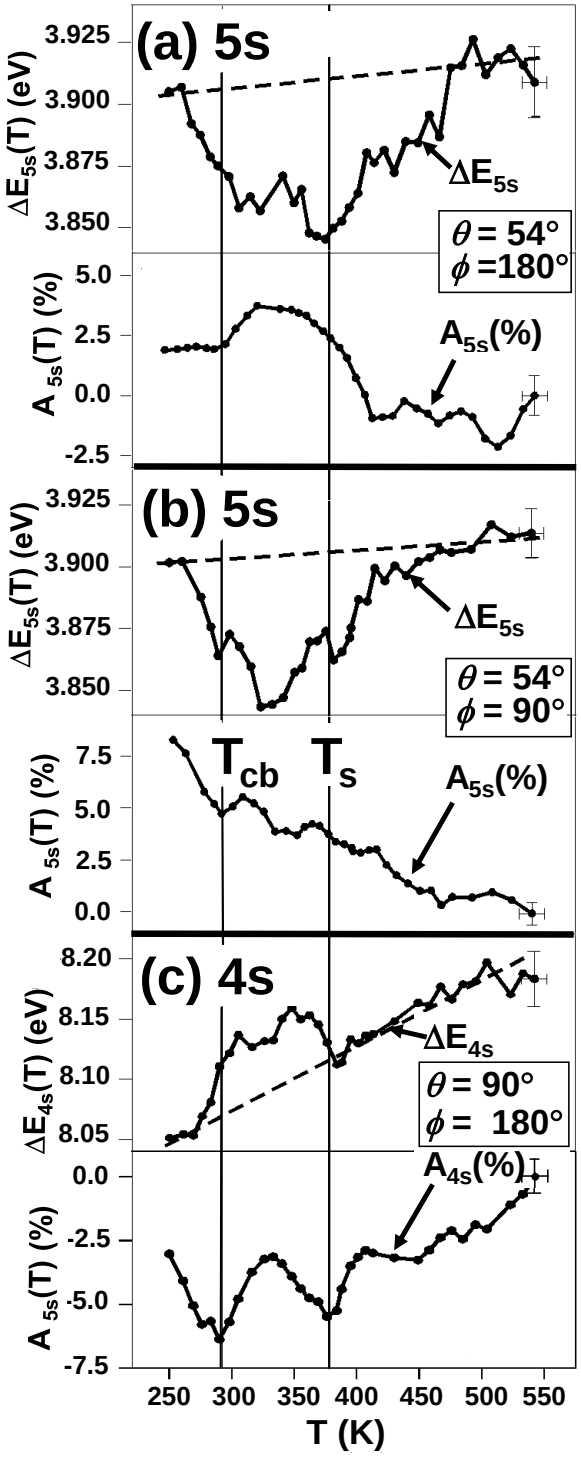


Figure 2: The dependence of the 5s and 4s s-level multiplet splitting and associated intensity asymmetry A (see definition in text) on temperature, for (a),(b) the Gd 5s spectra, for emission along two directions, and (b) the Gd 4s spectra, for emission along a third emission direction. The positions of the bulk curie temperature, T_{cb} and the second surface transition temperature T_s are also indicated.



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