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The ferromagnetic to paramagnetic transition in nickel studied by angular-resolved photoemission from single crystals

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Photoemission measurements ($\hbar\omega = 16.8$ eV and $\hbar\omega = 21.2$ eV) on the three high-symmetry faces (111), (100), and (110) of nickel have been performed. Specifically the temperature of the sample was varied to measure both the ferromagnetic and the paramagnetic state. The results obtained cannot be interpreted within the Stoner-Wohlfarth band model of ferromagnetism, if a value 0.3–0.5 eV of the exchange splitting is valid. However, a model, based on an intra-atomic exchange interaction, acting on the itinerant d electrons, is capable of explaining the data.

I. INTRODUCTION

Recently interest has once again been focused on the validity of the Stoner-Wohlfarth theory of ferromagnetism for Ni, especially with regard to the magnitude and temperature dependence of the so-called exchange splitting ΔE_{ex} (the energy separation between minority and majority electron bands). New electron-spin polarization (ESP) measurements on Ni by Eib and Alvarado[1] show a negative-spin polarization from Ni(100) and Ni(111) surfaces within 0.05 eV of the threshold. Earlier ESP measurements by Bänninger *et al.*[2] on polycrystalline samples showed always a positive polarization, however, with a larger energy window (0.4 and 0.8 eV within threshold). According to Eib and Alvarado these measurements do not contradict each other but are inconsistent with the Stoner-Slater-Wohlfarth band theory of magnetism.[1] On the other hand, Wohlfarth,[3] using a simple square model of the density of states, and Smith and Traum,[4] allowing only direct transitions in a more realistic band structure, did qualitatively *foresee* the new ESP results within the band model of ferromagnetism and offered also explanations of the old results. That the new results are consistent with the band model of ferromagnetism has, in a comment on the Eib and Alvarado paper,[1] once again been pointed out by Wohlfarth.[5]

Electron-spin polarization measurements of field-emitted electrons from the Ni(100) surface by Landolt and Campagna[6] have given results which agree with theoretical calculations[7,8] and also are considered[6] to agree with those of Eib and Alvarado,[1] even though in comparing such results one should keep in mind the large differences with regard to the nature of the excitations involved.[7,9] The ESP of field-emitted electrons has been shown to vary drastically with the emitting surface,[9,10] i.e., with the direction in $\vec{k}$ space probed. Both positive and negative polarizations P have been obtained as, for instance, in the measurement of Landolt *et al.*[11] Positive polarization was obtained in a tunneling experiment by Tedrow and Meservey.[12] All these results can be interpreted *within* a band model of ferromagnetism as was also pointed out by Landolt *et al.*[11] although a quantitative comparison is difficult to make due to the large differences in the s and d tunneling probabilities.[7] It is, however, important to point out that in none of these experiments can the exchange splitting be directly determined and in none has the exchange-splitting variation with temperature been (or can be) determined. [A measurement well above T_c was performed by Landolt and Campagna[6] yielding the result $P = 0.0 \pm 0.2\%$ which is thought to be due to a contamination of the surface rather than due to a variation of the exchange splitting. The extreme sensitivity of the polarization results to contaminants[13] makes these experiments very difficult to perform. Recently, Landolt and Campagna[14] have also demonstrated that demagnetization of a Ni(100) surface occurs upon hydrogen adsorption. In view of this we also think that the result of Chrobok *et al.*,[15] who actually find a P that follows the saturation magnetization, could not be considered as conclusive.]

Photoemission measurements on polycrystalline samples of Ni have been reported by Pierce and Spicer,[16] by Rowe and Tracy[17] (on cesiated Ni), and by Petersson *et al.*[18] (including also Fe) all using different photon energies. In these measurements one has been looking for the effect on the electron-energy distribution curve (EDC) of an exchange splitting assumed to vary in temperature in a similar way as the magnetization. The results obtained have been essentially the same: the EDC does not change appreciably when passing the Curie temperature. A similar conclusion but based on a weak argument was drawn by Nguyen *et al.*[19] from angular-resolved measurements

on Ni(100) above T_c.

The reason for doing the same type of measurement again but angular resolved and on single crystals is twofold.

Pro primo: with polycrystalline samples the EDC reflects an angle-integrated measurement, and this means that all direct transitions ($\vec{k}$ conserved) between bands separated by $\hbar\omega$ in the reduced Brillouin zone will contribute to the EDC. This means that the EDC will represent the envelope of a number of transitions throughout the Brillouin zone modulated and broadened by matrix elements, hole-lifetime and momentum broadening, electron-electron scattering, and final-state effects,[20] and thus, shifts in a separate transition could be more or less hidden. These effects should be particularly important in the case of Ni since the EDC from a polycrystalline sample fits very badly a calculated density of states.[18] Due to the ability of angle-resolved photoemission to, in principal, record one specific transition between two bands, as for instance demonstrated in the case of silver,[21] one should overcome this problem.

Pro secundo: one has to make clear that the EDC from nickel really represents a one-electron density of states. Thus this was the other reason to do these measurements since it has been proposed that the EDC does not reflect the single-particle density of states but rather is a result of a many-body interaction due to the high electron density at the Fermi energy.[22,23] Angle-resolved photoemission should be a good tool to separate these effects since a many-body effect would not be expected to vary drastically with emission angle, while the EDC reflecting the single-particle density of states might.

II. EXPERIMENTAL

We have performed photoemission measurements on the three high-symmetry faces (111), (100), and (110) of single-crystal nickel. Specifically we varied the temperature of the sample as to measure on both the ferromagnetic and paramagnetic state. The spectrometer used for this purpose consists of an ultrahigh-vacuum chamber reaching a base pressure of less than 10^{-10} Torr, equipped with a moveable small hemispherical electrostatic analyzer.[24] The relative energy resolution ($\Delta E_{1/2}/E$) of the analyzer was approximately 1%. As light source we used a differentially pumped, cold cathode resonance lamp operated on He or Ne. When operated the pressure in the chamber rose to $(1-2)\times 10^{-9}$ Torr due to the noble-gas flow. The angle of acceptance represents a rectangle of dimensions $\pm 1°$ by $\pm 3°$. The single crystals were oriented within $\pm 2°$, electropolished and cleaned *in situ* by argon bombardment ($\sim$650V, 10 $\mu A/cm^2$, $\sim$15 min) and subsequent annealing ($\sim$500 °C, 30–60 min). All the surfaces were easy to clean, one to two cycles of Ar sputtering and annealing would produce a clean surface as defined by the criterion that further cleaning would not change the EDC.

We recorded the EDC well above and well below T_c for two photon energies, $\hbar\omega = 16.8$ eV and $\hbar\omega = 21.2$ eV, and for each $\hbar\omega$ at emission angles $\theta = 0°$ and $\theta = 30°$ towards [111] from the (100) face, towards [100] from the (111) face, and towards [100] from the (110) face. The angle of incidence of the light was 45° and in the plane of emission. Each EDC presented is the sum of three measurements, all measurements taken in a series, typically like $T > T_c$, $T << T_c$, $T > T_c$, etc. The temperature for the high T's would change by approximately 60 K during a measurement but was always above 400 °C and thus well above T_c. The heating was shut off when the measurements started since we used a filament type of heater and did not want the magnetic fields from this device to interfere with our measurements. In certain cases we also recorded the variation of the EDC with temperature. The slight changes obtained in the EDC when varying the temperature are reversible. For this reason we believe the amount of bulk contaminants diffusing to the surface to be small.

III. RESULTS AND DISCUSSION

The results obtained for electron emission perpendicular to the surfaces, i.e., in the symmetry directions, agree well with those of Heimann and Neddermeyer[25] when the same photon energy and a similar light incidence ($\phi = 75°$) was used. When the angle of incidence was changed to $\phi = 45°$ (the angle used in the present measurements) slight intensity changes were observed.

We first consider the results with respect to the question of the EDC representing direct transitions in the single-particle band structure. There are strong indications that this is the case. The angular variation of our EDC's when leaving the symmetry direction is large for the (111) and (100) surfaces, see Figs. 1–4, as it might well be in a direct photoemission model. If the many-body interaction, as suggested by Kemeny and Shevchik,[23] was entirely responsible for the shape of the EDC the angular variation would not be this drastic. Also, Pessa[26] has lately disputed the large role of many-body interactions in forming the broad $2p$ levels as described by the model of Kotani and Toyozawa,[27] the model which also forms the base for the arguments of Kemeny and Shevchik,[23] and instead attributed the broadening to a multiplet splitting of the core-hole state.

The results of Heimann and Neddermeyer[25] along the symmetry direction have, at least for the (111) and (100) surfaces, been interpreted in terms of transitions from a band structure of the initial states.

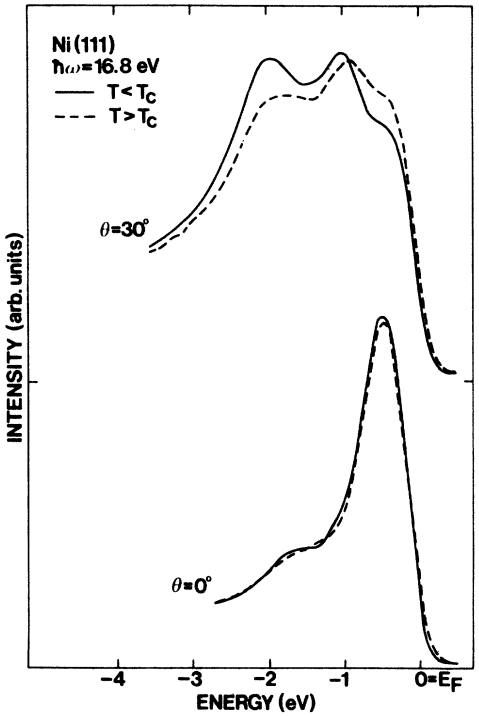

FIG. 1. Angular-resolved EDC's (AREDC) from a Ni(111) surface with $\hbar\omega = 16.8$ eV. θ defines the emission angle. Note especially the increase of intensity at $\theta = 30°$ for elevated temperatures.

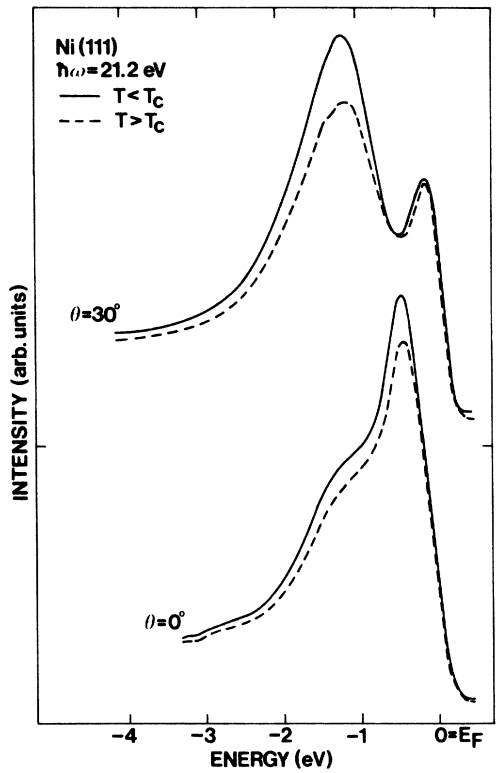

FIG. 2. AREDC's from a Ni(111) surface with $\hbar\omega = 21.2$ eV. Note the somewhat smaller width of the structure close to E_F at $T > T_c$ for the $\theta = 30°$ spectrum.

Smith *et al.*[28] concludes that their results from a Ni(100) crystal are consistent with a bandlike description. Also interesting to note is that results obtained with x radiation from polycrystalline samples of iron despite a bad agreement between EDC and the density of states, with a proper choice of parameters describing such effects as lifetime broadening and final-state effects, can be fitted with good agreement to such a modified theoretical single-particle density of states.[29] Thus, the conclusion from our own angular-dependent results, Figs. 1–4, supported by the recent publications mentioned, must be that it is reasonable to expect the photoelectron energy distribution to reflect a single-particle band structure. This is important to have established before we make an interpretation of our temperature-dependent measurements since otherwise we would not have a straightforward way of detecting the effects of a varying exchange splitting. However, it is not necessary for us to make an assignment in terms of a band structure of an observed transition or to be able to explicitly measure the exchange splitting, since, from whatever *d* band our transition occurs the initial energy would be shifted if ΔE_{ex} becomes zero above T_c. In such a case one should also be able to give a rough estimate of ΔE_{ex} by measuring the shifts.[17] As is seen from the band structure[30] in, for instance, the Γ-L direction, Fig. 7, the minority band closest to the Fermi energy would be lowered in energy by 0.15–0.25 eV depending on the value of ΔE_{ex}.[31]

The most conspicuous feature when comparing the EDC's above and below T_c is the variation in intensity, at most occasions a decrease with increasing T. In two cases, an increasing intensity of the main structures is seen: the high-energy structure in the EDC from Ni(111), $\theta = 30°$, $\hbar\omega = 16.8$ eV, Fig. 1, and the main peak in the Ni(110), $\theta = 30°$, $\hbar\omega = 21.2$-eV spectrum, see Fig. 6. Table I shows the intensity changes between $T << T_c$ (corresponding to a saturation magnetization of approximately 90% of the maximum value) and $T > T_c$. Within the band model, with a variation of ΔE_{ex} with temperature, one should expect to see intensity changes, both positive and negative, due to the fact that when the band moves in energy, the energy and $\vec{k}$-conservation rules will move the transition to take place somewhere else in the Brillouin zone, and thus, for a specific direction a peak could, in principle, completely disappear (the final state *s-p* bands can be considered to be stable in energy). The change of intensity due to this effect would cease above T_c since then the initial bands would also be stable in energy. We have followed the intensity variation as a function of temperature in the range

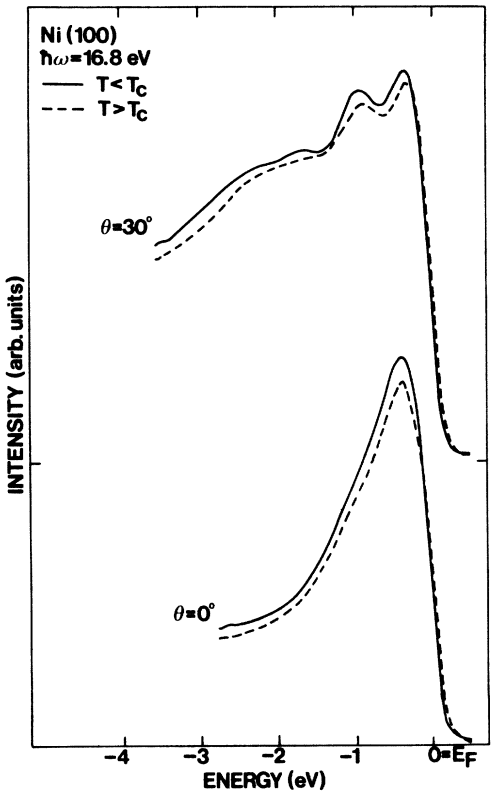

FIG. 3. AREDC's from a Ni(100) surface with $\hbar\omega = 16.8$ eV. For $\theta = 0°$ the upmost 10% of the structure is somewhat sharper peaked at the higher temperature.

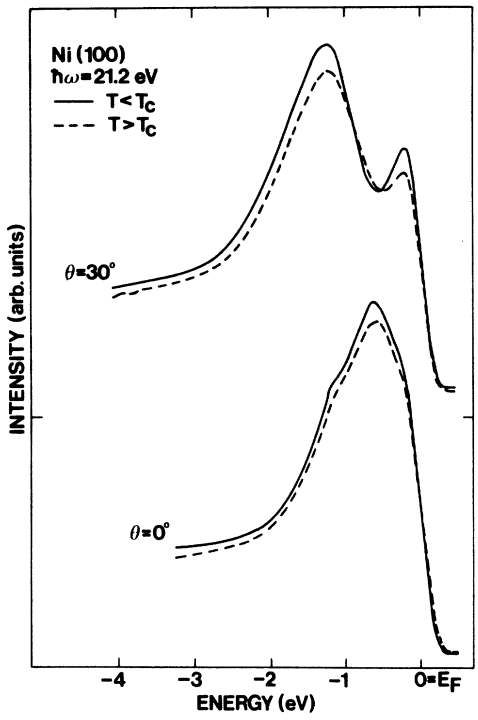

FIG. 4. AREDC's from a Ni(100) surface with $\hbar\omega = 21.2$ eV. The intensity decrease at the higher temperature for the structure close to E_F in the $\theta = 30°$ spectrum could be explained by a movement of the initial band across the Fermi energy.

$T \approx 0.65 T_c$ up to $T \approx 1.30 T_c$. The result for Ni(100), $\theta = 0°$, $\hbar\omega = 16.8$ eV is shown in Fig. 8, where the normalized intensity change is plotted versus temperature. The same behavior was obtained in all cases where such a measurement was done. It is thus seen that there is no drastic change in the rate of intensity variation around T_c; rather we expect this temperature dependent ΔI to be due to an increasing electron-phonon interaction. A model based on an electron-phonon scattering of the excited electron can explain both positive and negative variation of the intensity, depending on the magnitude of the intensity of that particular final state $E_0(\vec{k})$ compared with the average intensity of excited electrons of the same E_0. Thus, an intense structure, well localized in $\vec{k}$ space, is likely to decrease in intensity with increasing temperature, whereas a low-intensity structure may increase in intensity. Examples of both extremes are given in Fig. 5, Ni(110), $\theta = 0°$, $\hbar\omega = 16.8$ eV and in Fig. 1, Ni(111), $\theta = 30°$, $\hbar\omega = 16.8$ eV, respectively. (Note that also the variation with $\vec{k}$ of the density of states at the energy E_0 will influence the intensity transfer in the EDC's. In our discussion above we have neglected this effect.) Another possible explanation of this temperature dependence in uv photoemission has recently been put forward by Williams *et al.*[32] They interpret results on Cu by means of an increasing share of phonon-assisted (indirect) photoemission compared with that of the direct photoemission. Our data are not conclusive in separating these models.

Another general trend in the results is that for higher temperatures any structure is slightly less stressed, that is, intensity is moved from the peaks to the valleys (in accordance with phonon scattering), and thus the full width of the peaks are somewhat larger at higher temperatures.

Energy shifts of the peaks (with an uncertainty of ±0.05 eV) are also given in Table I. As seen from the table there is a slight positive shift towards E_F in 50% of the peaks, whereas for the other 50% the shift is less than 0.03 eV or in one case slightly negative.

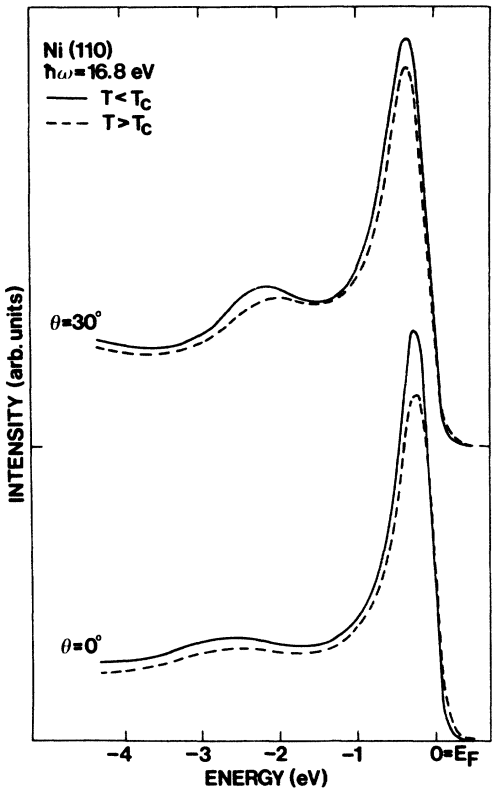

FIG. 5. AREDC's from a Ni(110) surface with $\hbar\omega = 16.8$ eV. Note the large intensity decrease of the sharp structure in the $\theta = 0°$ spectrum when the temperature is raised. The structure at $\theta = 0°$ is about 60% more intense than the structure at $\theta = 30°$.

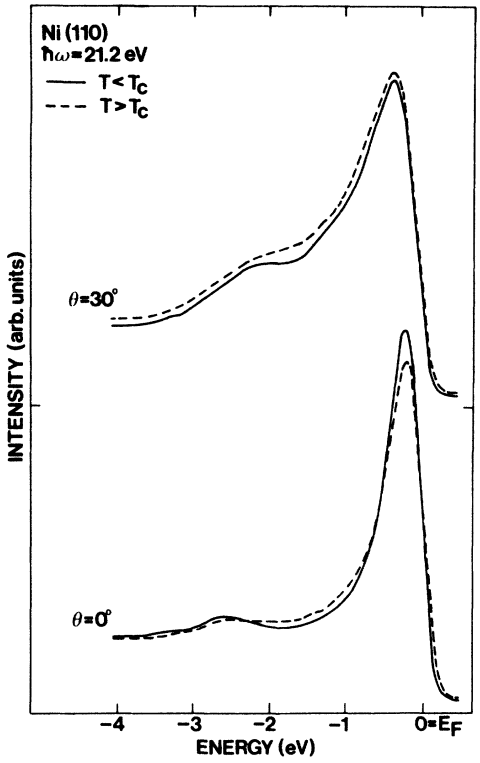

FIG. 6. AREDC's from a Ni(110) surface with $\hbar\omega = 21.2$ eV. Note the slight intensity increase at the higher temperature in the $\theta = 30°$ spectrum.

The band structure in the Γ-L direction suggests that the high-energy peak in the EDC from the [111] direction originates from the minority band closest to E_F. Thus, within the Stoner-Wohlfarth model, a negative shift should be expected when the temperature is raised. This is clearly not the case. An alternative designation of the high-energy peak is given by Heimann and Neddermeyer[25] who suggest that it originates from the high density of majority spin electrons at $L_3\uparrow$ (through a surface emission process). This would imply a positive energy shift which would probably to some extent be neutralized by the thermal expansion of the crystal[17] which would tend to decrease the bandwidth. If this interpretation, within the Stoner-Wohlfarth model, is correct the value of the exchange splitting should probably be less than 0.2 eV since the effects of band movement due to the thermal expansion and the changing exchange splitting experimentally seem to have canceled. Only in one case there are shifts which are of the expected absolute value to fit the change in the band structure if the exchange splitting depends on the magnetization. Unfortunately, the magnitude of these shifts [Ni(111), $\theta = 30°$, $\hbar\omega = 16.8$ eV, Fig. 1] is very uncertain since the intensity changes of these overlapping peaks also will influence the peak positions. For certain structures there is a slight sharpening of the top of the peak (i.e., for the upmost 10%) see, e.g., Fig. 3. In the case of Ni(100), $\theta = 30°$, $\hbar\omega = 21.2$ eV, Fig. 4, this could be accounted for by a band movement across the Fermi energy. However, in general the overall changes in features are small. Thus we think it is clear, under the condition that the band structure is responsible for the structures in the angular resolved EDC's from single crystals of Ni (through direct transitions or surface photoemission), that the band model, with an exchange splitting of the order of 0.3–0.5 eV which varies as the magnetization is not in accordance with our data even though one or two of the 12 different set of measurements can be explained within such a model. If the band model is valid this would have been evident as larger energy shifts of the peaks in our EDC's. A much smaller exchange splitting than what is generally accepted would explain the

TABLE I. The intensity and energy changes of the most pronounced structures in Figs. 1–6 as obtained when the temperature was raised from $T << T_c$ to $T > T_c$.

		Ni(111)		Ni(100)		Ni(110)	
		$\hbar\omega = 16.8$ eV	$\hbar\omega = 21.2$ eV	$\hbar\omega = 16.8$ eV	$\hbar\omega = 21.2$ eV	$\hbar\omega = 16.8$ eV	$\hbar\omega = 21.2$ eV
$\phi = 45°$	$\theta = 0°$						
	Intensity change (%)	−1	−12	−6	−5	−19	−9
peak 1[a]							
	Energy[b] change (eV)	+0.05	±0.00	−0.05	+0.10	+0.05	±0.00
$\phi = 45°$	$\theta = 30°$						
	Intensity change (1%)	+11	−1	−4	−11	−9	+3
peak 1[a]							
	Energy[b] change (eV)	-	±0.00	+0.05	±0.00	±0.00	±0.00
	Intensity change (%)	−3	−18	−4	−8		
peak 2[a]							
	Energy[b] change (eV)	+0.15	±0.00	+0.05	+0.05		
	Intensity change (%)	−13					
peak 3[a]							
	Energy[b] change (eV)	+0.15					

[a]The numbers refer to the most pronounced structures counted from E_F.
[b]±0.05 eV.

results, especially the sharpening of the peaks if one assumes that each experimental peak consists of transitions from both spin-up and spin-down electron bands and that these merge to a common initial energy for high temperatures.

IV. CONCLUSION

We do not rule out an itinerant electron model as such but if the exchange splitting is of the order of 0.3–0.5 eV, which seems very reasonable whatever model is used,[31] it is not following the same temperature dependence as the magnetization. However, there seems to be a slight temperature dependence in the experimental results and thus a much weaker temperature dependence for the exchange splitting than for the magnetization (or just a smaller exchange splitting) would be in accordance with the results. Slater,[32] e.g., has theoretically pointed out that the exchange splitting should have nothing to do with the Curie temperature.

The idea of itinerant electron states with localized magnetic moments on each site varying in magnitude and direction was developed already in the early '60's[34] but seems to have been overlooked by experimentalists. However, there does exist experimental support for this idea. Grimvall,[35] in an analysis of thermodynamic data, concludes, for instance, that the magnetic moments seem to persist even in the liquid phase. Gunnarsson[36] states that the Curie temperature should mainly be determined by the interaction between the localized moments since a calculation based on the Stoner parameter gives too large a T_c. We also want to mention the measurements on the work function variation with temperature on single crystals of nickel which do not show any anomalies around T_c.[37]

It is interesting to point out that a temperature-dependent ESP measurement cannot easily distinguish between a true Stoner-Wohlfarth model, and the model of the localized magnetic moments since it measures an average of the ESP over some volume and energy. The ideal experiment is, of course, an

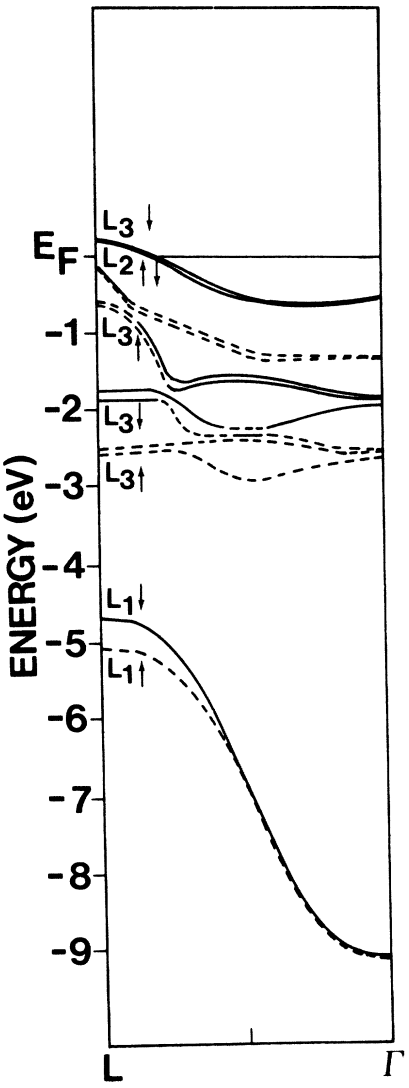

FIG. 7. Energy bands in the Γ-L direction as given by Wang and Callaway (Ref. 30). Dashed lines give the majority spin bands, and the full lines give the minority spin bands.

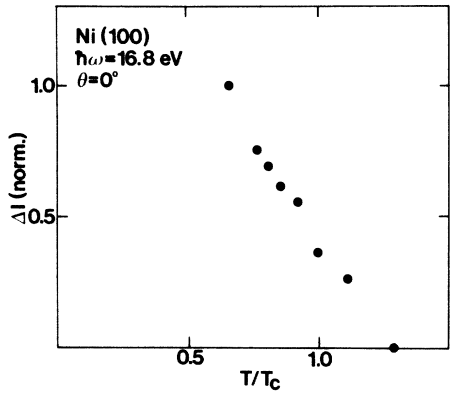

FIG. 8. Normalized intensity change (i.e., change of the peak height) vs temperature, of the main structure in the AREDC from a Ni(100) surface with $\hbar\omega = 16.8$ eV and $\theta = 0°$. The uncertainty in ΔI in each point is about 0.07.

angular-resolved photoemission experiment on single crystals using low-photon energies ($\lesssim$11.6 eV) combined with an energy-discriminated ESP measurement. The photoemission experiment itself is, however, insensitive to the long-range magnetic order.[38]

Thus, we think that an intra-atomic exchange interaction, acting on the itinerant d electrons explains not only our data but also the ESP data of both photo- and field-emitted electrons.

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